MOLECULAR MECHANICS CALCULATIONS ON SOME PHOSPHINE OXIDE METAL COMPLEXES IN AQUEOUS AND ORGANIC SOLVENTS

by

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ABSTRACT

Molecular mechanics calculations were done on tetrahedral phosphine oxide zinc complexes in simulated water, benzene and hexane phases using the DREIDING II force field in the BIOGRAF molecular modeling program. The SUN workstation computer (SUN_4c, with SPARK station 1 processor) was used for the calculations. Experimental structural information used in the parameterization was obtained from the September 1989 version of the Cambridge Structural Database.

Steric and solvation energies were calculated for complexes of the type $ZnCl_2(R_3PO)_2$. The calculations were done with and without inclusion of electrostatic interactions. More reliable simulation results were obtained without inclusion of charges.

In the simulated gas phase, the steric energies increase regularly with number of carbons in the alkyl group, whereas they go through a maximum when solvent shells are included in the calculation. Simulated distribution ratios vary with chain length and type of chain branching and the complexes are found to be more favourable for extraction by benzene than by hexane, in accord with experimental data. Also, in line with what would be expected for a favorable extraction, calculations without electrostatics predict that the complexes are better solvated by the organic solvents than by water.

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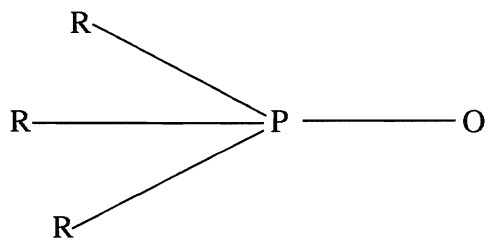
1 INTRODUCTION

I. PHOSPHINE CHEMICALS AND THEIR USES

The project is centered around a class of phosphine oxide chemicals whose general form is shown in the figure below:

Phosphine Oxide Chemical

('R' = alkyl or aryl group)



Used in single form or mixed with similar phosphine chemicals, with various combinations of 'R' group types and in a variety of organic solvents, the phosphine oxide chemicals can be used to:

1. Clean up metal or organic pollutants from waste waters and

2. Extract or recover metals from ores in hydrometallurgical processes.

Examples and uses (as well as possible uses) of commercially available phosphine oxide chemical extractants of the form shown above are given in table 1.1; these chemicals are made by Cyanamid Canada at their Welland plant in Niagara Falls, Ontario.

Examples Of Commercially Available Phosphine Oxide Chemicals

COMPOUND	COMPOSITION OR STRUCTURE	APPLICATIONS OR POTENTIAL USES
I **(CYANEX 921)**	**R_3PO** Where: R = $CH_3(CH_2)_7$- , *n*-octyl	1. All applications as for compound III below. 2. Recovery of Re and Li 3. Possible separation of many metals as in table 1.2
II **(CYANEX 925)**	**R_2R^*PO** Where: R* = $CH_3(CH_2)_7$- , *n*-octyl R = $[CH_3CH(CH_3)_2CH_2$-$\underset{\displaystyle CH_3}{\underset{\vert}{CH}}$-$CH_2$-	Demonstrates superior selectivity for the range of metals that are usually extracted by Cyanex 921
III **(CYANEX 923)**	**Mixture of:** **R_3P0, R_2R^*PO,** **R_2R^*PO and R^*_3PO** Where: R = $[CH_3(CH_2)_7$-- *n*-octyl R* = $[CH_3(CH_2)_5$-- *n*-hexyl	1. Organic Solutes Recovery: *--carboxylic acid, phenols and ethanol.* 2. Inorganic Solutes Recovery: *--removes As impurities from Cu electrolytes.* *--extraction of U from ores.* *--Nb-Ta Separation.*

Table 1.2 below shows metals which are known (4) to extract well with trioctylphosphine oxide extractant ; oxidation states and favorable acid systems for extraction are also indicated in Table 1.2 as obtained from reference (4).

Table 1.2: Metals Known To Extract Well With Trioctylphosphine Oxide

Ti	**V**	**Cr**	**Mn**	**Fe**		**Cu**	**Zn**	**Ga**	**Ge**	**As**
IV	V	VI	VII	III		II	II	III	IV	III
a c	a	a c	a b c	a		a	a	a	a	a
Zr	**Nb**	**Mo**	**Tc**				**Cd**	**In**	**Sn**	**Sb**
IV	V	VI	VII				II	III	IV	III, V
a b	a	a b c	a c d e				a	a	a	a a
Hf	**Ta**				**Pt**	**Au**	**Hg**			**Bi**
IV	V				IV	III	II			III
a b	a				a	a	a			b
Ce										
IV										
b c										
Th		**U**	**Np**	**Pu**						
IV		VI	IV	IV, VI						
a b		a b	b c	a b a b						

Acid systems from which favourable or selective extraction can be effected as indicated in the table are as follows:

a. HCl *b.* HNO_3 *c.* H_2SO_4 *d. HBr* *e.* H_3PO_4

II. MOLECULAR MECHANICS

II.A MOLECULAR MECHANICS, AB INITIO AND SEMI-EMPIRICAL CALCULATION METHODS

There are three major approaches commonly used in computing molecular strucuture, energies and other molecular properties. These methods are: (1) Empirical molecular mechanics, (2) *ab initio* quantum mechanics and (3) Semi-empirical quantum mechanics .

Molecular mechanics derives its basic theory from the Born-Oppenheimer approximation discussed in most introductory books on quantum mechanics; the Born-Oppenheimer approximation states that one can separately treat the motions of the nuclei and electrons. Thus molecular mechanics treats a molecule as an array of atomic nuclei distributed on a Born-Oppenheimer potential energy surface whereby the energy surface is a function of only the nuclear positions; using equations similar to the classical equations of motion, nuclei of the structure are moved about the potential energy surface with the aim of finding the positions which will give the minimum energy for the structure. The energy calculated by molecular mechanics is called steric energy, a summation of the various potential energies for bonds, bond angles, torsional angles, non-bond interactions and other features in the molecule. In comparison, strain energy is not restricted to molecular mechanics alone and is described with respect to a strain-free molecule. The conventional definition of strain energy states that the strain energy is the difference between the heats of formation of the molecule tested and a totally strain-free molecule of the same constitution. Thus where the formation energy is to be calculated by molecular mechanics,

it is often treated as a sum of the calculated steric energy and the bond or group energy increments of a strain-free molecule.

In *ab initio* quantum mechanical methods, the Schrödinger equation is first solved for a given trial nuclear configuration, with explicit treatment of electrons; the nuclear configuration is then systematically adjusted so as to minimize the energy of the molecule. This cycle is repeated until an energy minimum for the molecule is reached. A truncated wave function (the basis set) is often used in the calculations so as to simplify the calculations and reduce the amount of computation time.

Semi-empirical quantum mechanical methods are a simplified version of the *ab initio* quantum mechanical methods; semi-empirical quantum mechanical methods have the objective of reducing the large amount of computation time needed in *ab initio* calculations by omitting certain families of electron correlation integrals from the Schrödinger equation. In order to compensate for the omitted integrals, some of the numbers used in the calculations are consequently adjusted so that the semi-empirical quantum mechanical results will better match the *ab initio* or experimental results.

II.B STRENGTHS AND WEAKNESSES OF MOLECULAR MECHANICS IN RELATION TO AB INITIO AND SEMI-EMPIRICAL CALCULATION METHODS

All three methods for calculating molecular properties (molecular mechanics, *ab initio* and semi-empirical) have the ability to predict the chemical behavior of a known or unknown molecular species. However, molecular mechanics has the advantage over either

ab initio or semi-empirical methods in that molecular mechanics requires less computation time when the three calculation methods are applied to the same structure; furthermore, molecular mechanics can be applied to larger molecules while *ab initio* and semi-empirical methods require an excessive amount of computer time when applied to larger molecules. The main limitation of the molecular mechanics calculation method is that molecular mechanics requires a lot of experimental data to be used in defining the model molecule to which the calculated results can be fit; no experimental data need necessarily be available before *ab initio* methods could be applicable.

A limitation applicable to all the three molecular calculation methods is that crystal packing or solvent effects and other bulk properties may constrain the geometries of the molecule under experimental observation such that molecular calculations which are done on an isolated molecule may fail to reproduce the properties of a molecule in a bulk matrix. However, more sophisticated software now allows for inclusion of solvent shells, thus giving molecular mechanics significant advantages over other calculation methods in the present project.

II.C HISTORY OF MOLECULAR MECHANICS

Ideas about the nature of bonds between bonded atoms and of Van der Waals forces between non-bonded atoms have long been known in chemistry; molecular mechanics can be thought of as originating from such ideas about forces between bonded and non-bonded atoms (5). The mathematical basis of molecular mechanics has been provided by the

fundamental formulations used in vibration spectroscopy.

As early as 1930, Andrews (6) presented some basic ideas about molecular mechanics concerning equilibrium or 'natural' values for molecular geometries and strain energies of deformed molecules. Sixteen years later, in 1946, the first serious attempts to apply molecular mechanics ideas were made by Hill (7), and by Ingold and co-workers (8) as well as by Westheimer and Mayer (9).The work by these three independent groups of workers provided the foundation on which later developments of molecular mechanics methods came to be based.

By 1961, Hendrickson (10) was able to do molecular mechanics calculations on medium ring cycloalkanes using a computer. However, a major step forward in computer based molecular mechanics calculations came in 1965 when Wiberg (11) wrote an energy minimization computer program which would optimize crude starting coordinates in order to calculate the actual molecular geometry. Later work in the development of molecular mechanics energy minimization computer programs has its origin in the program written by Wiberg.

Most of the early molecular mechanics applications were in the field of organic chemistry and much work has been done in this field. However, partly due to the difficulty of applying molecular mechanics techniques to complex heteronuclear systems, application of molecular mechanics techniques to inorganic systems did not progress as fast as with organic systems (12). This is in spite of the fact that the first quantitative application of

molecular mechanics to transition metal systems came as early as 1959 when Corey and Bailar (13) calculated the strain energies of some simple coordination complexes with five- and six- membered rings.

Of late, molecular mechanics applications to inorganic systems have become increasingly important (12). For example, deviation from the equilibrium value for the metal-ligand distance (a function of metal size) has been correlated to the strain energy in order to determine the reasons for selectivity of some open-chain and macrocyclic ligands for metals of different sizes (14). Also, solvation energy has been shown to be a significant factor in the selectivity of the 18-crown-6 macrocyclic host species for sodium and potassium guest ions (15). Furthermore, Hancock et al. (16-18) have obtained good agreement between the change in calculated steric energy (ΔE) and the change in experimental energy of formation ($\Delta[\Delta H]$) that occur when the steric and formation energies of free ligands are compared to the steric and formation energies of the corresponding complexes. A recent review by Hancock (19) covers a wide range of molecular mechanics calculations which have recently been applied to problems in coordination chemistry.

There have been some brief and simple molecular mechanics calculations on phosphine oxide ligands and related compounds using the ALCHEMY modeling program, without explicit solvent inclusion (2). Results from this modeling work suggest that Cyanex 924 (Tris-2,4,4-trimethylpentylphosphine oxide) has a less favourable steric energy than Cyanex 925 (Bis-2,4,4-trimethylpentyl-*n*-octylphosphine oxide) but a more favourable steric

energy than Cyanex 471X (Tri-*iso*-butylphosphine sulfide); Cyanex 925 and Cyanex 471X are commercially available while Cyanex 924 cannot be prepared in commercial quantities due to a 'significant degree of steric crowding' (20). Since the commercially unavailable Cyanex 924 has a more favourable steric energy than the commercially available Cyanex 471X, Gastrone et al. (2) concludes that there is a solution to the preparation of Cyanex 924.

The future outlook is that molecular mechanics calculations will increasingly become more important in coordination chemistry as molecular mechanics force fields become more refined; the use of specialized functions to treat metal centers (21) and the inclusion of more atom types (including metals) in some force fields (22) is an indication of this upcoming importance of molecular mechanics calculations in coordination chemistry.

II.D MOLECULAR MECHANICS CALCULATION APPROACH

II.D.1 Mechanical Model Of A Molecule

What we initially need to do in molecular mechanics calculations is to represent a molecule in terms of a model whose nature can be visualized as a mechanical object consisting of an array of connected or unconnected 'masses'; the behavior of the mechanical model is described by a set of force laws and force constants. The model so defined can then be used to determine and predict the behavior of the representative molecule.

Definition and development of the model for a given molecule is done in such a way that the model will reproduce experimental facts about the molecule; how good the model is in representing the properties of the molecule under study will mainly be determined by how

well it can reproduce the experimental facts and how many experimental facts it can reproduce.

II.D.2 Molecular Mechanics Potential Functions And Force Fields

Each of the force laws (and the associated force constants in each force law) is called a potential function. The force laws and constants that are used in describing the mechanical model constitute a force field.

Mathematically, a force field can be expressed as a summation of all the necessary force laws, with each force law energy term being summed over all the individual interactions (equation 1.1):

Molecular mechanics force field expression:

$$E_T = \Sigma E_r + \Sigma E_\theta + \Sigma E_\phi + \Sigma E_{vdw} + \Sigma E_\varphi + \ldots\ldots \quad (1.1)$$

Energy terms indicated in equation 1.1 are the ones commonly included in most force fields and a description of each of these energy terms is as follows:

E_T = total steric energy for the molecule.

E_r = bond-stretch energy contribution to the total energy; describes the energy associated with stretching a bond from an equilibrium value.

E_{θ} = angle-bend energy contribution to the total energy; describes the energy associated with bending a bond angle from an equilibrium value.

E_{ϕ} = torsion energy contribution to the total energy; describes the energy barrier to rotation about a bond.

E_{vdw} = Van der Waals nonbond energy contribution to the total energy; describes the forces between neutral atoms not bonded to one another.

E_{φ} = electrostatic nonbond energy contribution to the total energy; describes the electrostatic energy associated with the charges (and permanent dipoles) in the molecule.

The interaction between atoms involved in hydrogen bonding are described by the *Hydrogen Bond Potential Function.* The *Inversion Potential Function* is used to describe the energy involved in planarising a central atom. Some force fields will include *Cross Terms* in order to reproduce energy effects which depend on both bond length and bond angle yet a few other force fields have *Specialized Potential Functions* for special functions such as the treatment of the metal center.

A listing of the forms of potential functions commonly found in most force fields is given on the following page:

BOND STRETCH POTENTIAL FUNCTIONS

Harmonic $$E_r = 1/2K_r (r - r_o)^2 \quad (1.2)$$

Morse $$E_r = D_O \left(e^{-\alpha\{ [r - r_o] - 1\}} \right)^2 \quad (1.3)$$

Cubic $$E_r = 1/2k_r (r - r_o)^2 (1 + d[r - r_0]) \quad (1.4)$$

ANGLE BEND POTENTIAL FUNCTIONS

Theta expansion $$E_\theta = 1/2K_\theta (\theta - \theta_0)^2 \quad (1.5)$$

MM2 Angle potential $$E_\theta = 1/2K_\theta (\theta - \theta_0)^2 [1 + d_1(\theta - \theta_o)^4] \quad (1.6)$$

Schleyer potential $$E_\theta = 1/2K_\theta (\theta - \theta_0)^2 [1 + d_2|\theta - \theta_o|] \quad (1.7)$$

TORSIONAL POTENTIAL FUNCTION

$$E_\phi = \sum_{n=1}^{6} 1/2K_\phi (1 - d_3 \cos [n\phi]) \quad (1.8)$$

VAN DER WAALS POTENTIAL FUNCTIONS

Lennard-Jones 12-6 $$E_{vdw} = \varepsilon_O \left([r_o / r]^{12} - 2 [r_o / r]^6 \right) \quad (1.9)$$

Exponential-6 $$E_{vdw} = \varepsilon_O ([\{6 / \gamma - 6\} e^{\gamma(1 - r/r_o)}] - [\{6 / \gamma - 6\} \{r_o / r\}^6]) \quad (1.10)$$

For equations 1.2 to 1.10;

E_r, E_θ, E_ϕ and E_{VDW}= respective bond-stretch, angle-bend, torsion, and Van der Waals energy terms

K_r = bond-stretch force constant

K_θ = angle-bend force constant

K_ϕ = constant for torsional barrier to rotation

r_0 = equilibrium bond length or Van der Waals separation at the minimum energy in a non-strained molecule

r = actual bond length or Van der Waals separation

θ_0 = equilibrium bond angle in a non-strained molecule

θ = actual bond angle

ϕ = displacement of dihedral angle from ideal value

D_o = bond energy; $\alpha = (K_r D_O)^{1/2}$; n = periodicity; ε_o = depth of the potential well

d = cubic correction term (usually d = -2 for MM2 and MMP2 force fields)

d_1 = sectic term = $7 \times 10^{-8} (180 / \pi)^4$ radians^4

d_2 = cubic angle factor = - 0.55 (radian)

d_3 = phase factor; -1 if cis conformation energy is maximum torsional energy and +1 if cis conformation energy is minimum torsional energy

γ = scaling factor (related to the steepness of the repulsive part of the Exponential-6 expression); the value of '2' in the Lennard Jones 12-6 expression is an adjustable number which correlates the attractive and repulsive parts of the potential function.

Several force fields enjoy wide use and are commercially available. The DREIDING force field (22) is a general purpose force field applicable to a wide range of chemical, biochemical and polymer systems; it does well in reproducing structural data for both organic and inorganic compounds including organometallic complexes.The generic MMX force fields (where the force field version number X = 1, P1, 2, P2 and 3) give good structures and energies for most organic molecules; The latest version, MM3 (23), uses one parameter set to treat saturated hydrocarbons, conjugated hydrocarbon systems, aromatic heterocycles and other related compounds. AMBER (24) and CHARM (25) force fields were designed for biological and protein molecules.

II.D.3 Molecular Mechanics Constants

Both experimental data and calculated values are used as sources of information for defining the molecular model. Types of such information and their sources is given in this section.

The Cambridge Structural Database (CSD) As A Source Of Information: The Cambridge Structural Database (26) is a computer based databank containing critically evaluated scientific numeric data on organic and inorganic structures. These data are obtained from x-ray or neutron diffraction structure determinations. The central location of the Cambridge Structural Database in Canada is in Ottawa and the database can be accessed through terminals all over the country.

Among other things, the database can be used to search for specific molecular

structures, perform geometric calculations and provide bibliographic information about a compound. Data on equilibrium geometries of a molecule are usually obtained from a statistical analysis of the experimental geometries of similar compounds retrieved from the Cambridge Structural Database.

Other Sources Of Information: Bending and stretching force constants are obtained from either vibrational spectroscopy or previous force field studies on similar compounds. Torsional force constants are determined from experimental rotational barriers about bonds of interest in simple compounds.

The data required for determining the Van der Waals potential (ε_o) and the distance of minimum energy (r_o) for Van der Waals interactions come from Van der Waals potentials and radii of rare gases as determined from second virial coefficients (27) and molecular beam experiments (28). The numerical value of '6' in the attractive part of the Van der Waals potential function comes from the expression (1.22) which is used in evaluating the dispersion energy:

$$\text{dispersion} = -C_6 r^{-6} - C_8 r^{-8} - \ldots\ldots\ldots \qquad (1.22)$$

The numerical value for γ in the repulsive part of the Van der Waals potential function (where $\gamma = 12$ in most cases for the Lennard-Jones 12-6 potential) is determined by an empirical fitting process so as to reproduce the virial coefficient data of rare gases. The factor which correlate the attractive and repulsive parts of the Van der Waals potential functions

('2' for the Lennard-Jones 12-6 expression) is also evaluated by a fitting process whereby the calculated results are matched to experimental data on non-bonded interactions.

Atomic charges can either be calculated by *ab initio* methods, where this is possible, or obtained from charges of closely related compounds; the BIOGRAF modeling program has algorithms (29, 30, 31) which are capable of calculating charges.

Information on hydrogen bond strength (D_o), hydrogen bond distances (r_{AD}) and hydrogen bond angles (θ_o) may be obtained from experimentally determined values in the literature (32).

Parameter Optimization: The parameters used in the force fields often need to be adjusted (optimized) so that the molecular properties calculated by molecular mechanics best fit those determined by experiment. Stretching force constants are usually used as obtained from vibrational spectroscopy or other force field studies, with little or no modification. Bending force constants determined by experiment usually need to be scaled down. Torsional energy force constants of molecules are optimized by fitting the rotational barriers about bonds of interest in similar simple compounds. Non-strained equilibrium bond lengths and bond angles determined from analysis of geometric information from the database sometimes need adjustment to suit the force field being used. Optimization of Van der Waals parameters (ε_o, r_o and γ) may be done by an empirical derivation of Van der Waals curves in which the calculated Van der Waals curves are compared to the experimental data on crystal spacings (related to the Van der Waals distance) and sublimation energies (related to the Van der

Waals potential energy). Charge and hydrogen bond parameters are often optimized by adjusting the starting values so as to reproduce molecular properties such as dipole moments and solvation energies.

Parameter optimization can be done by inspection (that is by trial and error) in which one inspects for errors and makes adjustments as is necessary. Alternatively, the least squares standard method (33) can be used in parameter optimization; in this case, optimization involves a mathematical procedure whereby the parameters are varied by an iterative process until the sum of squares of all differences between calculated and experimental quantities reaches a minimum value. A third alternative method for parameter optimization is to use a combination of both the inspection and least squares standard method.

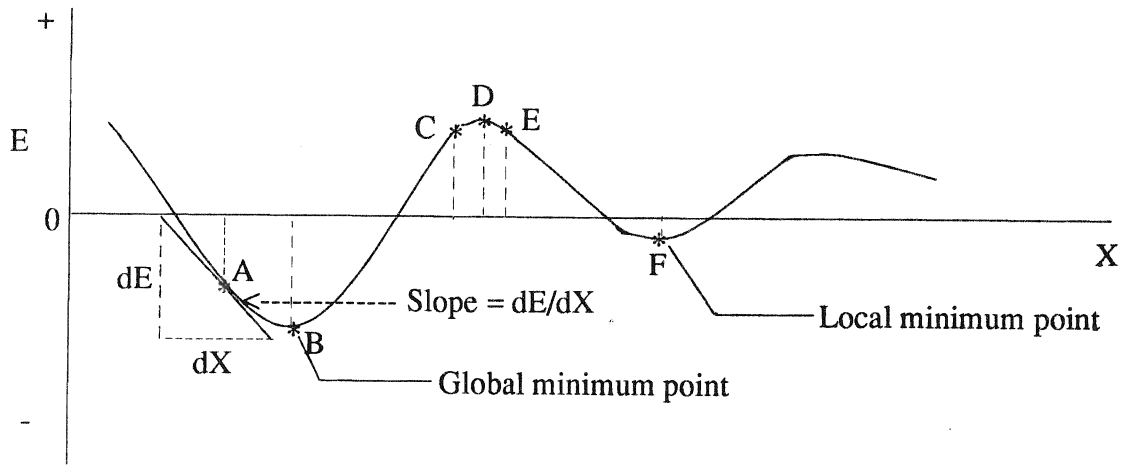
II.D.4 Molecular Mechanics Energy Minimization

Starting with some initial coordinates for the structure, the molecular mechanics energy minimization program will move the atoms of the molecule about the potential energy surface with the aim of finding a conformation in which the energy of the molecule is minimum; the minimized structure is expected to reproduce, among other things, the experimentally determined geometries and energies. The process of searching for an energy minimum of the model molecule is what is called 'minimization' in molecular mechanics.

To illustrate the mathematical principles of the energy minimization methods, we first consider the variation of the potential energy (E) with respect to movement in the direction of one of the coordinates (X) as illustrated in Figure 1.1. The first step in the calculation is to

determine the slope at the first trial position, say point A in Figure 1.1; having done this, the atom is moved by an amount proportional to the slope and in a direction that would yield a reduction in energy as determined by the sign of the slope. This calculation procedure is repeated a number of times (iteration) until the energy no longer decreases or until some pre-set minimum energy condition is met. The potential energy minimum for the molecular structure would then correspond to the atomic positions in which the derivatives or slopes of the potential energy with respect to all of the coordinates are simultaneously equal to zero for all atoms in the structure.

Figure 1.1: Variation Of Potential Energy With Respect To Variation In Atomic Coordinates



Simple search methods (generally known as steepest-descents or first derivative methods) make use of only the slope of the potential surface while the more sophisticated minimization methods (generally known as Newton-Raphson or second derivative methods)

utilize both the slope (first derivative) and the curvature (second derivative) of the potential energy surface.

Steepest-descents Minimization Methods: In the steepest-descents or simple search minimization methods (34), the slope is evaluated numerically or analytically; numerical determination of the slope is done by comparing the energy value at the first trial position (say A in Figure 1.1) to the energy value at the next position (say B in Figure 1.1) while the analytical determination of the slope involves evaluating the first derivative ($\delta E/\delta X$) of the potential energy surface with respect to the atomic coordinates.

Conjugate-Gradient (or 'Pattern Search') energy minimization procedure (35) can be looked at as an improvement on the steepest-descents method whereby the conjugate-gradient procedure makes use of the information concerning directions and size of motions of previous minimization steps as well information about the current gradient in order to determine the next step.

Newton-Raphson Minimization Methods: The mathematical basis of the more sophisticated Newton-Raphson methods (36) involves expanding the force field expression in a Taylor series and truncating after the second order term; the first derivative in the truncated Taylor series will measure the slope as in the steepest-descents method while the second derivative will determine the curvature or rate of change of the slope.

Comparison Of Energy Minimization Methods: Steepest-descents minimization is fast and reliable when one is far from the energy minimum but becomes slow when

approaching the energy minimum or when moving down a gentle slope. On the other hand, the conjugate gradient method works well when one is near an energy minimum but is less efficient (and often converges poorly) if starting with a poor geometry which is far from energy minimum.

Conjugate-gradient minimization often leads to convergence in fewer steps than minimization by the steepest-descents method. Fewer steps in the conjugate-gradient case are due to the fact that the conjugate-gradient makes use of information from the previous and current minimization steps in order to accelerate the motions near the energy minimum or down a gentle slope; the larger displacements for conjugate-gradient compared to steepest-descents also help to accelerate the motions in the conjugate-gradient minimizations.

Partly due to the small displacements, steepest-descents minimization can be useful in minimizing large changes caused by a few bad (or high energy) contacts in a crude starting geometry; in this way, steepest-descents method can be used in getting a crude starting geometry near to the energy minimum where the more sophisticated methods will work well.

Making use of second order information in the Newton-Raphson minimization methods increases the computational time for each iteration ; however, utilizing second derivative information in Newton-Raphson methods allows convergence in fewer steps than is the case with steepest-descents methods such that the total computational time required in Newton-Raphson methods is often less than that required in steepest-descents methods. Moreover, Newton-Raphson methods often allow convergence to lower energies than is the

case with steepest-descents.

Generally speaking, more sophisticated methods usually work well if one is near the energy minimum but do poorly when one is far away (5, 37); the less sophisticated methods work better if one is far from the energy minimum and become less efficient as minimization approaches the minimum value. Hence minimization procedures where the steepest-descents is first applied followed by Newton-Raphson technique (38) have shown better results than using either of the two minimization methods alone; combining the minimization methods has the advantage that each method is applied where it performs best (5).

The Problem Of Multiple Minima And Conformation Search Techniques: Positions B and F in Figure 1.1 are two possible energy minima for the one dimensional case; an atom starting at position C or A has a possibility of minimizing to position B down the slope while an initial structure starting at position E is likely to minimize to position F down the other slope; for the Newton-Raphson minimization methods, the structure may even 'minimize' to point D (Figure 1.1) where the energy is maximum because the Newton-Raphson pre-set convergence criteria of $\delta E/\delta X = 0$ can also be satisfied at point D. Up to now, there is still no known mathematical method of determining whether a structure has minimized to the best or lowest energy minimum. Conformation search techniques have been developed to search for lower energy conformations; among such conformation search techniques are the annealed molecular dynamics (39), systematic dihedral angle search and Monte Carlo searching in dihedral space (40).

Searching with molecular dynamics algorithms essentially involves calculating forces acting on every atom using Newton's third law of motion (F = ma; F = force, m = mass and a = acceleration) and then moving the atoms in response to the forces. The Verlet algorithms (41, 42) are used to integrate Newton's equations of motion. In annealed dynamics, the temperature starts at an initial value and increments by a specified amount at specified intervals to a final temperature; the temperature then increments back to the initial temperature to complete the cycle. For annealed dynamics on BIOGRAF, the structure with the lowest potential energy from the annealing cycle is minimized after the end of the cycle and then written to the trajectory file. During the dynamics run, the velocities of the atoms are rescaled to match the temperatures; the velocities in turn are related to the acceleration ('a') in Newton's third law of motions for the evaluation of atomic forces. In this way, the forces acting on atoms can be varied in a systematic way so as to overcome energy barriers. Running dynamics at hotter temperatures allows the system to overcome conformation energy barriers more easily though too hot a temperature results in almost all the conformations being high in energy such that the dynamics run will no longer give much useful information when the temperature is too high.

Systematic and Monte Carlo dihedral search techniques are used to search for low energy torsional angles; the main objective in this case is to find likely starting points for low-energy conformations. One or more dihedral angles can be varied simultaneously in the search and a specified number of searched conformations written out in the order of

increasing energy. Systematic dihedral search varies the torsional angles as specified by the user while the Monte Carlo dihedral search adjusts torsional angles at random.

III. PROBLEM DEFINITION AND PROJECT OBJECTIVES

III.A Problem Definition

Although commercial applications of the phosphine chemicals do exist as given in Tables 1.1, there are no rapid ways of screening such chemicals for their effectiveness and selectivity as extraction agents. For example, we need to know the steric and electrostatic effects that the various possible 'R' group substituents have on the stability of the various metal complexes in solution; furthermore, we need to know the solvent--complex interactions in as far as they relate to the stability of the extractable metal complex in various solvents.

We proposed to use recently developed molecular modeling programs with force field energy minimization to screen the phosphine oxide chemicals for their effectiveness (and possibly selectivity) as extraction agents for metals; we further proposed to use models that could explicitly include solvation shells for both aqueous and organic phases so that the calculated solvation energies could be related to experimentally determined extraction coefficients. Computational studies which prove promising would then be subjected to laboratory evaluations in later studies outside this project.

III.B Project Objectives

The project objectives were as follows:

1. To theoretically explore the energies of phosphine oxide metal complexes in different solvents as a way of designing ligands for metal extraction in different solvents and as a way of investigating the extractability of phosphine oxide metal complexes in different solvents.
2. To explore the usefulness of molecular mechanics calculations in studying solvent extraction systems involving metal complexes of phosphine chemicals.

The DREIDING II force field(22) on BIOGRAF software was used in all calculations.

2. CAMBRIDGE STRUCTURAL DATABASE (CSD) SEARCHES AND ANALYSIS

I. DATABASE SEARCH AND GEOMETRY CALCULATIONS

Phosphine oxide information for determining equilibrium bond distances and angles used in molecular mechanics calculations was retrieved from the September 1989 version of the Cambridge Structural Database (26); the master file searched contained 73,893 entries.

Structures from the database were retrieved using the program CONNSER while bibliographic information on the structures was extracted using BIBSER program. The ligands and metal complexes retrieved from the database were the ones containing the fragment shown below:

Search Fragment:

$(C)_3$-P-O-[M]

Specifications for the above search fragment were as follows:

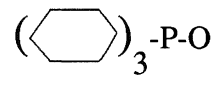
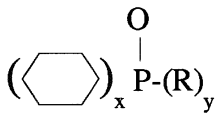
'O' atom bonded to one or two non-hydrogen atoms,

M = metal atom.

Number of hydrogens on C atom = 1,2 or 3

277 structures matched the search criteria. Table 2.1 show the number of ligand and metal complex structures located for each ligand type:

Table 2.1: Summary Of CSD Searches For Phosphine Oxide Structures

Class	Ligand Type	Number of structures located	
		Ligands	Complexes
I	$(Ph)_{3-}P\text{-}O$ Ph = phenyl group	41	104
II	$(R)_{3-}P\text{-}O$ R = alkyl group	5	20
III	$(Ph)_x\overset{O}{\overset{\vert}{P}}\text{-}(R)_y$ X + Y = 3	68	37
IV		0	1
V	 X + Y = 3	1	0

RETRIEVE program was used to retrieve numeric data associated with the database reference codes created by CONNSER or BIBSER. This was followed by a geometry calculation on the retrieved data using the program GEOM78. The following geometries were the ones calculated:

C-P, P-O and O-M distances,

C-P-C, C-P-O and M-O-P angles and

M-O-P-C torsions.

For the purpose of our molecular mechanics work, the structures retrieved were screened for random and systematic errors; the criteria used for accepting a CSD entry in our molecular mechanics calculations were as follows:

(i) metal complexes with triphenyl- or trialkyl- phosphine oxide ligands only; no combination of different types of trialkyls or a combination of triphenyl and trialkyl in one ligand group.

(ii) A crystallographic R factor of less than or equal to 0.085 .

(iii) Structures were not to be affected by disorder.

(v) Atomic coordinates were to be available both in the database and the literature.

Structures which passed the screening process were 83 in number. Bibliographic and geometric information for the screened structures is given in Appendix III.

II. ANALYSIS OF CSD DATA

II.A ESTIMATION OF P-C EQUILIBRIUM DISTANCE

The histograms on the following page (Figures 2.1 and 2.2) show the P-C bond distance distributions for the respective triphenylphosphine oxide and trialkylphosphine oxide complexes in the appendix (Tables III.3 and III.4). Each square in Figures 2.1 and 2.2 represents three P-C bond distance entries for the associated CSD data. As per standard practice in other analyses of crystallographic information (26, 43), values which deviated significantly from the main cluster were excluded.

Figure 2.1 for triphenylphosphine oxide complexes show a cluster of P-C bond distances between 1.76 Å and 1.84 Å. Not enough data were available to adequately characterize the P-C equilibrium bond distance in trialkylphosphine oxide complexes (Figure 2.2). A similar analysis of phosphine oxide CSD data by Allen et al. (43), in which both phenyl- and alkyl phosphine oxide complexes were analysed together , found the mean and median P-C distance values to be 1.791 Å and 1.794 Å respectively; these values are within our range of P-C distances for triphenylphosphine oxide complexes. A P-C equilibrium distance of 1.815 Å was subsequently found to be suitable for our DREIDING II force field calculations on triphenyl- and trialkyl phosphine oxide complexes. Initially, DREIDING II had a default P-C equilibrium distance of 1.620 Å which was far below that observed from the CSD data; this value of 1.620 Å is also far below the P-C equilibrium distances of 1.828 Å and 1.848 Å as used by Allinger's MM force fields (45, 46, 47).

Figure 2.1: P-C Bond Distance Distribution For Triphenylphosphine Oxide Complexes

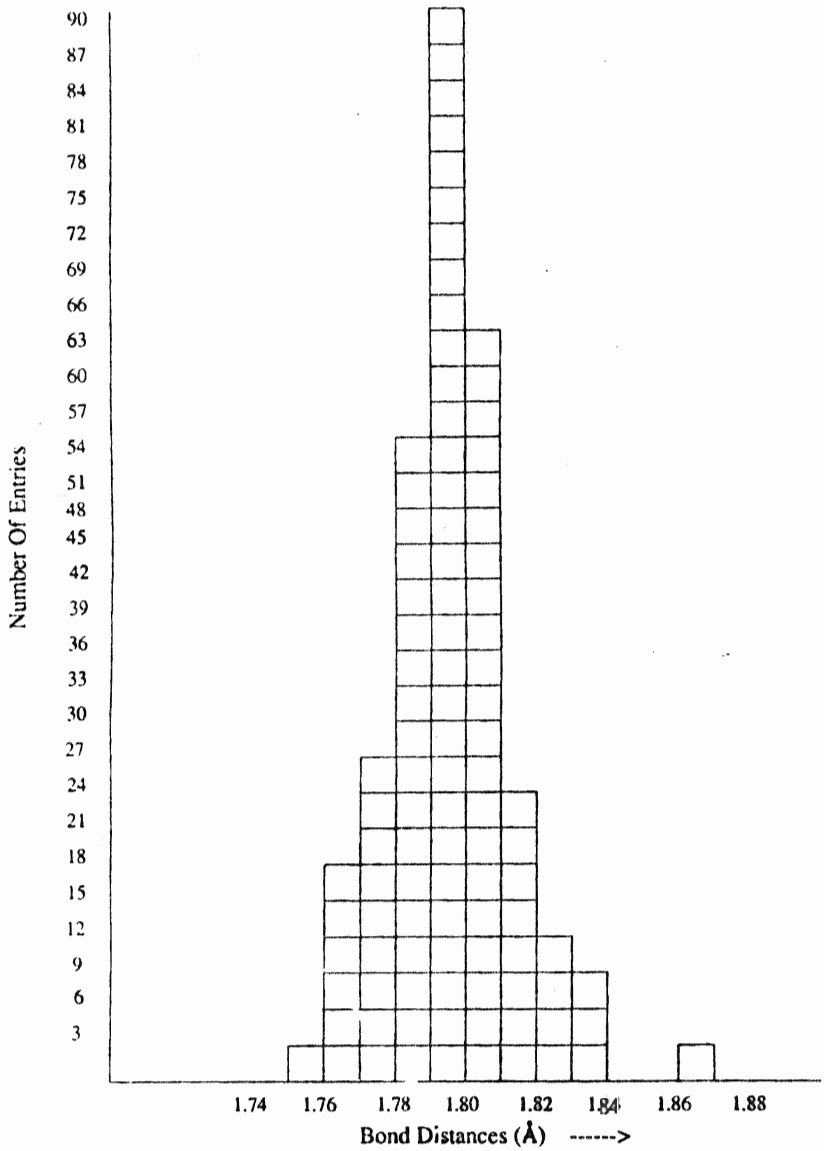
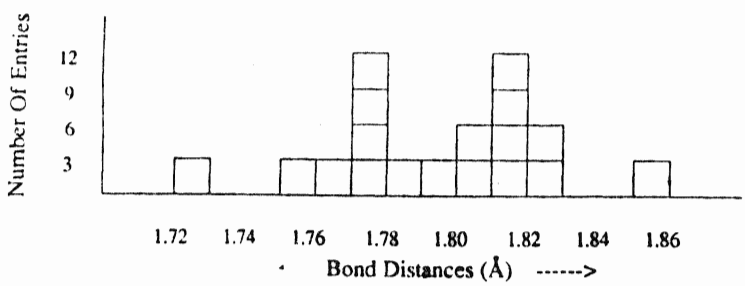


Figure 2.2: P-C Bond Distance Distribution For Trialkylphosphine Oxide Complexes



II.B ESTIMATION OF P-O EQUILIBRIUM DISTANCE

The histograms in Figures 2.3 and 2.4 show the P-O bond distance distribution for the respective triphenylphosphine oxide and trialkylphosphine oxide complexes from the CSD search. Each square in Figures 2.3 and 2.4 represents one P-O bond distance entry for the respective data on triphenylphosphine oxide and trialkylphosphine oxide complexes in Tables III.3 and III.4. Again, values which deviate significantly from the main cluster are not included in the histograms.

Figure 2.3 for triphenylphosphine oxide complexes showed a cluster of P-O bond distances between 1.47 Å and 1.53 Å. Again, not enough data was available to adequately characterize the P-O equilibrium distances in trialkylphosphine oxide complexes (Figure 2.4). A similar analysis of phosphine oxide CSD data by Allen et al. (43), in which both phenyl- and alkyl phosphine oxide complexes were analysed together, found the mean and median P-O distance values to be 1.506 Å and 1.505 Å respectively; these values are also within our estimated range of P-O distances for triphenylphosphine oxide complexes. Therefore replacing the default DREIDING II P-O equilibrium distance of 1.540 Å by a P-O equilibrium distance of 1.505 Å gave calculated P-O bond distances which agreed well with experimental values (see chapter 4).

Figure 2.3: P-O Bond Distance Distribution For Triphenylphosphine Oxide Complexes

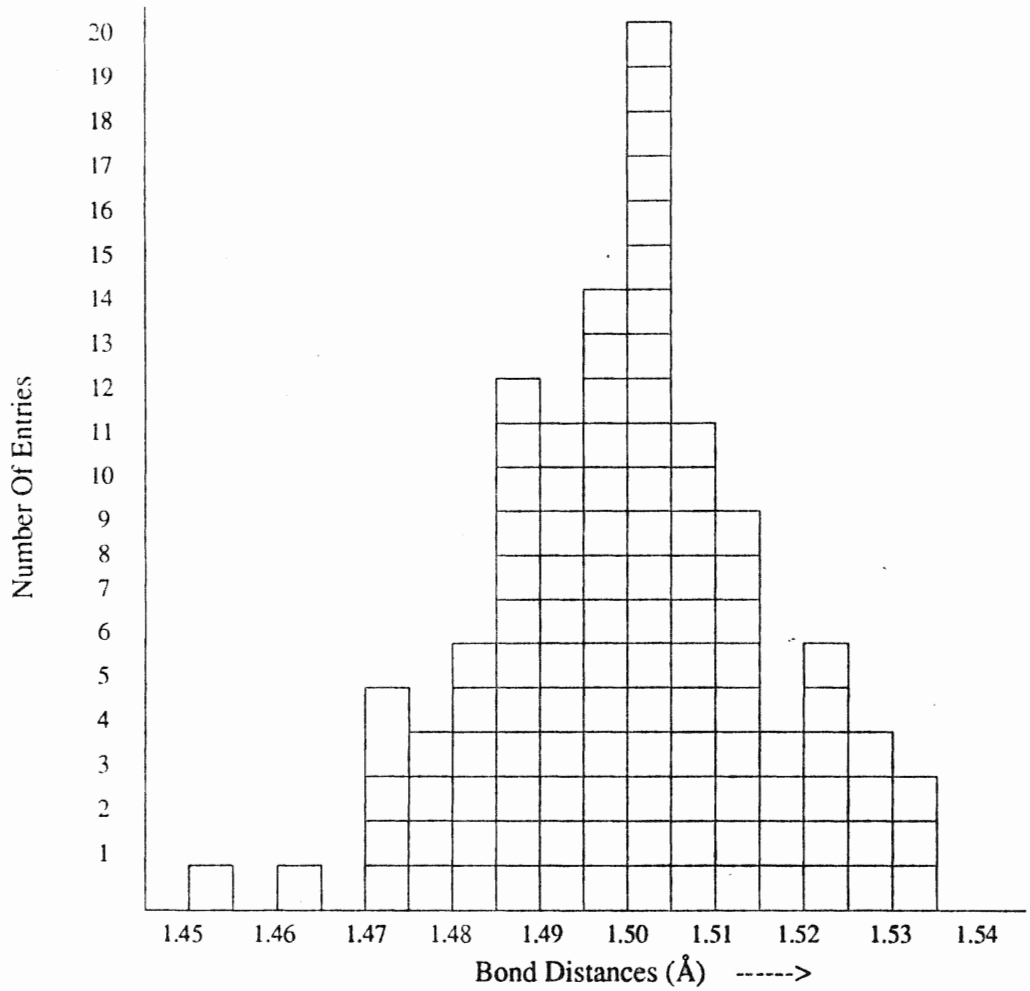
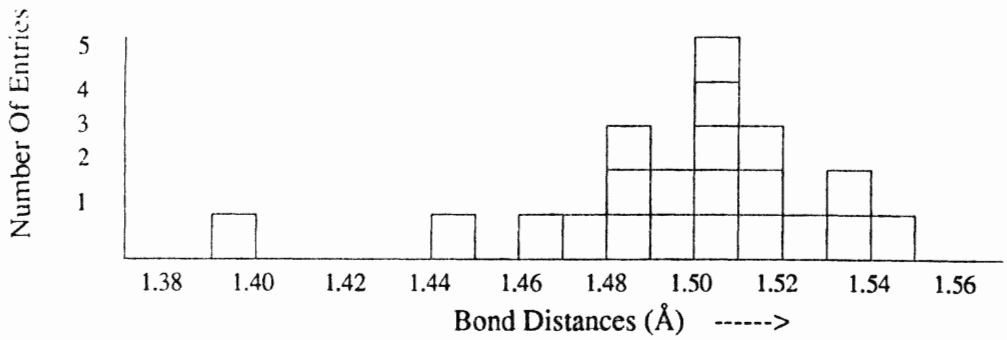


Figure 2.4: P-O Bond Distance Distribution For Trialkylphosphine Oxide Complexes



II.C ESTIMATION OF C-P-C EQUILIBRIUM ANGLE

C-P-C bond angle distributions for triphenylphosphine oxide and trialkylphosphine oxide complexes are shown in Figures 2.5 and 2.6. Each square in Figures 2.5 and 2.6 represent three C-P-C bond angle entries for the associated CSD data in the appendix (Tables III.5 and III.6). Values which deviate significantly from the main cluster are excluded from Figures 2.5 and 2.6.

The histogram for C-P-C angle distribution has a broad base with an approximate normal distribution (Figure 2.5); a cluster of C-P-C bond angles between 105.0^{o} and 111.0^{0} is evident in Figure 2.5. Not much can be deduced about the distribution of trialkylphosphine oxide C-P-C bond angles from the few scattered data points in Figure 2.8, though a small cluster of C-P-C bond angles between 108.0^{o} and 109.0^{o} is evident. Therefore using a value of 108.5^{0} for C-P-C equilibrium angle of triphenylphosphine oxide and trialkylphosphine complexes, in place of the default DREIDING II C-P-C equilibrium angle of 93.0^{o}, gave C-P-C geometries which were in close agreement with the experimental C-P-C angles obtained from the CSD.

Figure 2.5: C-P-C Bond Angle Distribution For Triphenylphosphine Oxide Complexes

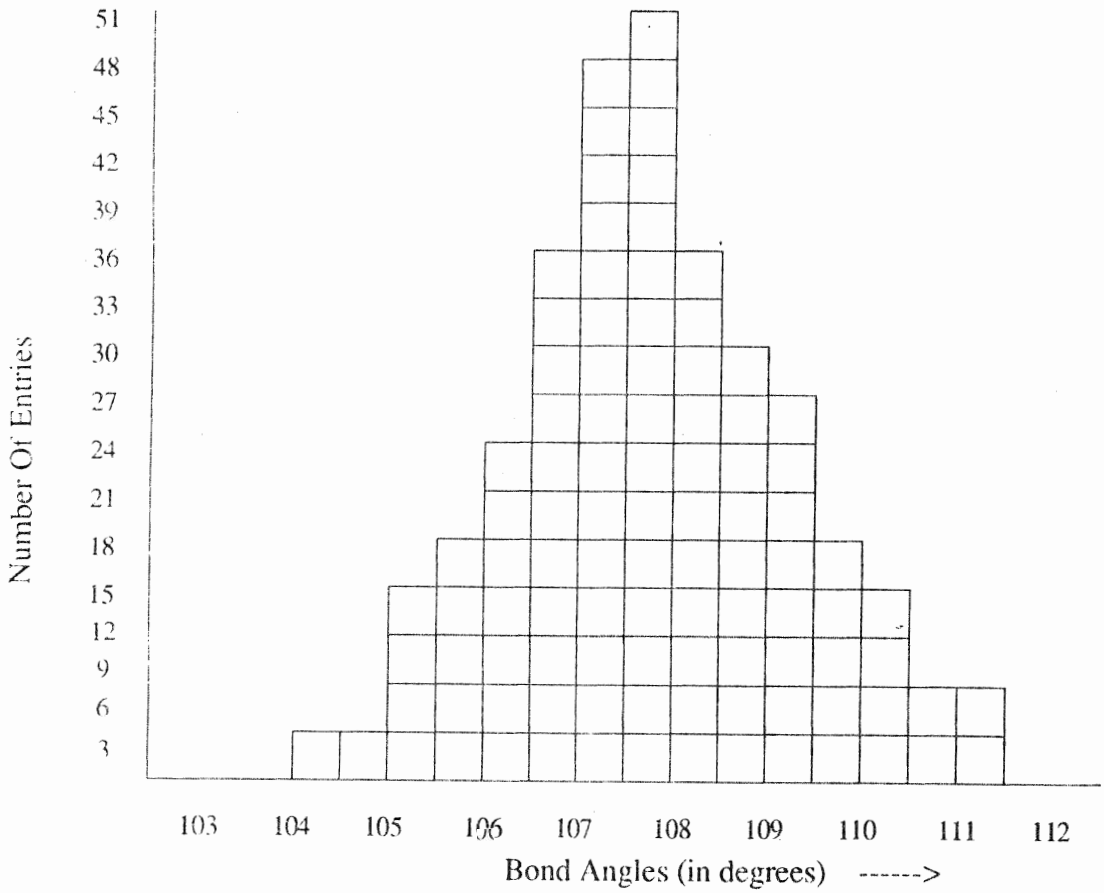
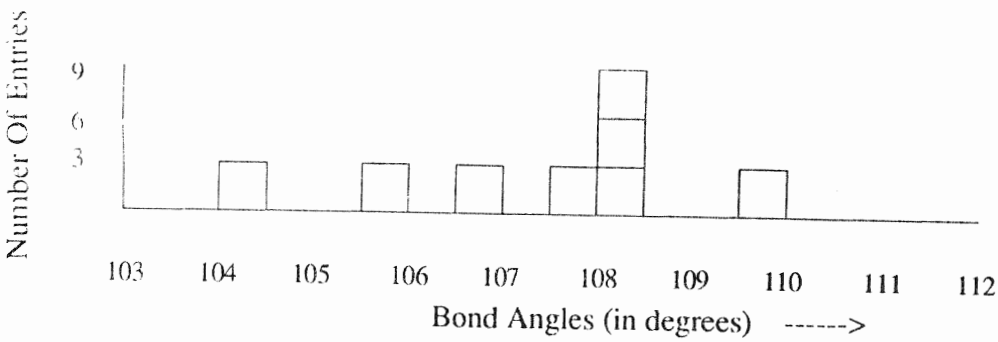


Figure 2.6: C-P-C Bond Angle Distribution For Trialkylphosphine Oxide Complexes



II.D ESTIMATION OF O-P-C EQUILIBRIUM ANGLE

Figures 2.7 and 2.8 show the histograms for the O-P-C bond angle distributions in the respective triphenylphosphine oxide and trialkylphosphine oxide complexes in Tables III.5 and III.6. Each square in Figures 2.7 and 2.8 represent three O-P-C bond angle entries for the associated CSD data in the appendix. Values which deviate significantly from the main cluster are not included in the figures.

As is the case with C-P-C angle distribution in triphenylphosphine oxide complexes, the histogram for O-P-C angles in triphenylphosphine oxide complexes (Figure 2.7) has a broad base with an approximate normal distribution centered around 111.0°. Though not enough data were available for trialkylphosphine oxide complexes, the few data points in Figure 2.8 also tend to fall between 110.0° and 113.0°. Hence a value of 111.5° for O-P-C equilibrium angle for triphenylphosphine oxide and trialkylphosphine complexes, in place of the default DREIDING II O-P-C equilibrium angle of 93.0°, resulted in O-P-C calculated angles which were in close agreement with the experimental O-P-C angles obtained from the CSD.

Figure 2.7: O-P-C Bond Angle Distribution For Triphenylphosphine Oxide Complexes

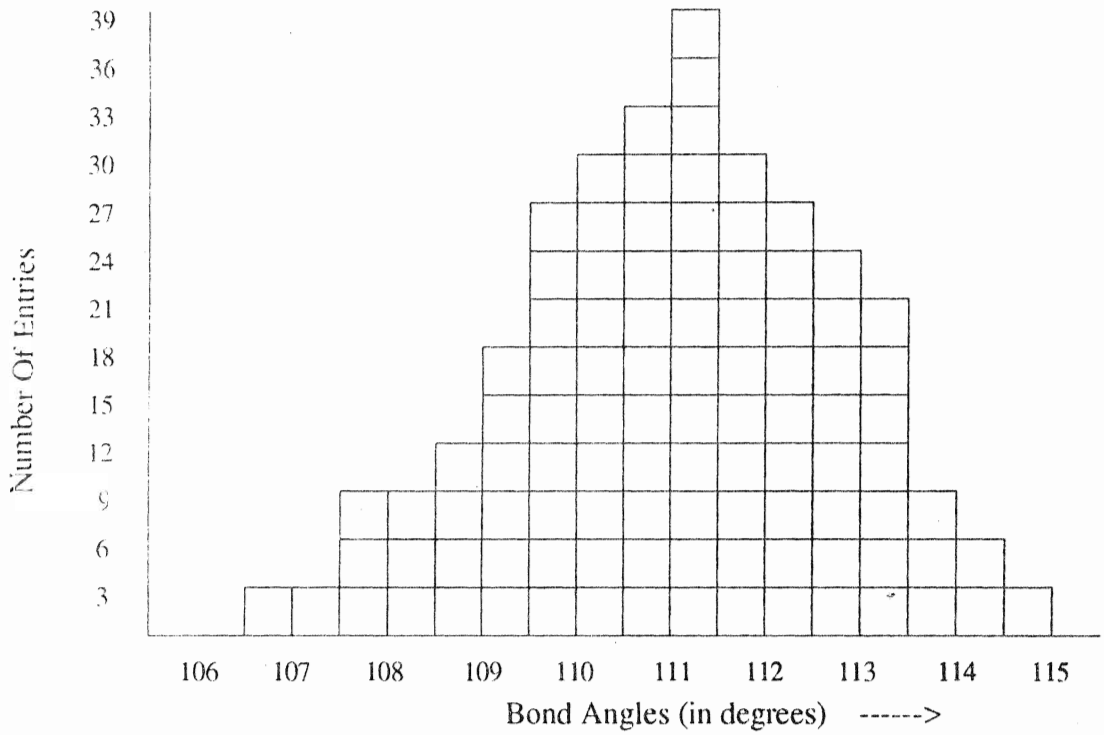
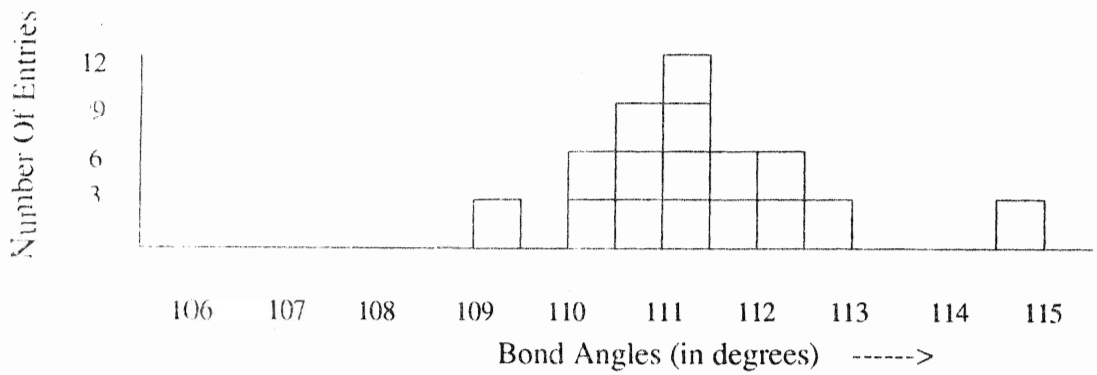


Figure 2.8: O-P-C Bond Angle Distribution For Trialkylphosphine Oxide Complexes



II.E ESTIMATION OF M-O-P EQUILIBRIUM ANGLE (M = ANY METAL)

The histograms in the respective Figures 2.9 and 2.10 were deliberately plotted irrespective of metal type or coordination number in order to get an idea about the general distribution of M-O-P angles in triphenylphosphine oxide and trialkylphosphine oxide complexes. Each square in Figures 2.9 and 2.10 represent one M-O-P bond angle entry for the respective data on triphenylphosphine oxide and trialkylphosphine oxide complexes in Tables III.5 and III.6.

For both triphenyl- and trialkyl phosphine oxide complexes, the M-O-P angles are widely spread out between 130^{o} and 180^{o} (Figures 2.9 and 2.10). Though no distinct cluster can be readily identified in both Figures 2.9 and 2.10, M-O-P angles in triphenylphosphine oxide complexes tend towards larger angles within the range of 130^{o} to 180^{o} while M-O-P angles in trialkylphosphine oxide complexes tend towards smaller angles within the same range of 130^{o} to 180^{o}. A fairly distinct cluster of M-O-P angles for triphenylphosphine oxide complexes shows up between 145^{o} and 170^{o} (Figure 2.9) while the few scattered data points for M-O-P angles in trialkylphosphine oxide complexes seem to fall between 130^{o} and 155^{o} (Figure 2.10). Through a systematic variation of the metal center angles and associated force constants, we found that an equilibrium value of 145.0^{o} for the Zn-O-P angle of the model complex (44) was successful in reproducing the experimental Zn-O-P geometries for both triphenylphosphine oxide and trialkylphosphine oxide complexes. Hence the default DREIDING II Zn-O-P equilibrium angle of 109.47^{o} was replaced by the value of 145.0^{o}.

Figure 2.9: M-O-P Bond Angle Distribution For Triphenylphosphine Oxide Complexes

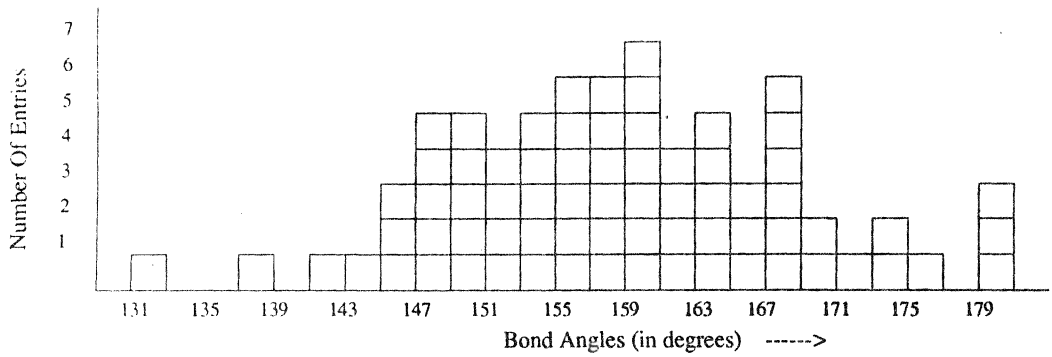
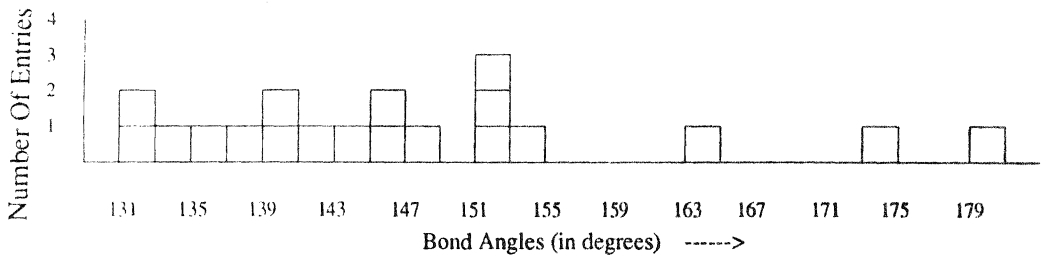


Figure 2.10: M-O-P Bond Angle Distribution For Trialkylphosphine Oxide Complexes

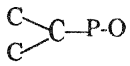
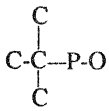
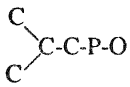
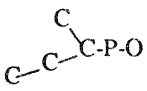
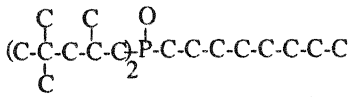
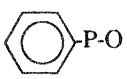


3. MOLECULAR MECHANICS CALCULATIONS

I. OUTLINE

The metal complexes modeled were tetrahedral zinc complexes with the general formula $ZnCl_2L_2$ where the ligand types 'L' are shown in Table 3.1 below:

Table 3.1: Phosphine Oxide Ligand Types Used In The Calculations

Ligand Type	Name	Abbreviation
-C-P-O	Trimethylphosphine oxide	TMPO
-C-C-P-O	Triethylphosphine oxide	TEPO
-C-C-C-P-O	Tri-*n*-propylphosphine oxide	TNPPO
-C-C-C-C-P-O	Tri-*n*-butylphosphine oxide	TBPO
-C-C-C-C-C-C-P-O	Tri-*n*-hexylphosphine oxide	THPO
-C-C-C-C-C-C-C-C-P-O	Tri-*n*-octylphosphine oxide	TOPO
	Tri-*sec*-propylphosphine oxide	TSPPO
	Tri-*tet*-butylphosphine oxide	TTPO
	Tri-*iso*-butylphosphine oxide	TIPO
	Tri-*sec*-butylphosphine oxide	TSBPO
	Bis-2,4,4-trimethylpentyl-*n*-octylphosphine oxide	TPOPO
	Triphenylphosphine oxide	TPPO

The zinc complexes were modeled in water, benzene and *n*-hexane solvents. Energy terms calculated were those for bond stretch, angle bend, torsions, Van der Waals, inversions, electrostatics and hydrogen bonding. Our main objective was to theoretically investigate the ligand and solvent effects on the distribution of tetrahedral zinc complexes between organic and aqueous phases during solvent extraction process.

II. COMPUTER FACILITIES

Molecular mechanics calculations were done using the DREIDING II force field (22) in the BIOGRAF (version 2.2) modeling program. BIOGRAF was installed on the SUN Workstation computer (SUN-4c, with SPARK Station 1 processor).

The SUN Workstation is a high performance workstation with 'mainframe equivalent' processing speed of 10 million instructions per second (10 MIPS). It is oriented towards applications in areas like Computer Aided Design (CAD) and graphics.

BIOGRAF is a general purpose modeling program for organic and inorganic structures. As many as seven force fields have been installed on our BIOGRAF program; these are DREIDING I and II (22), MM2 (45,46), MMP2 (47), CHARMM (25) AMBER and AMBERB (24). Force Field energy terms allowed on BIOGRAF are those for bond-stretch, angle-bend, torsion, inversion, Van der Waals, electrostatics and hydrogen bonding. There is a wide selection of potential functions on BIOGRAF; these include all the force field potential functions given in the introduction. The minimization algorithms available on

BIOGRAF are steepest-descents (34), conjugate-gradient (35) and Fletcher-Powell (48).

BIOGRAF allows explicit inclusion of a solvent shell around a molecular system as well as simulation of hydrogen bonding. BIOGRAF also has three charge calculation algorithms (Gasteiger (30), Q Equil (29) and Del Re (31)) and a provisions for calculating electrostatic energy as well as running dynamics of motions for atoms at constant or varying temperatures. Standard Verlet (42) and summed Verlet (41) are the two dynamics calculation programs available on BIOGRAF.

III. PARAMETERIZATION

The model compound to which the calculated geometries were fit during parameterization was dichloro-bis(triphenylphosphine oxide) zinc(II) (44). Parameter optimization was done by trial and error method and optimum values for many of the parameters are stated in the previous chapter.

Except where the default DREIDING II parameters deviated significantly from experimental values, no modification of the default DREIDING II parameters was made. Following below is a listing of the geometries for which it was found necessary to modify some or all of the associated parameters:

Bond distances: P-O, P-C, Zn-Cl

Bond angles: Zn-O-P, O-P-C, C-P-C, O-Zn-O, O-Zn-Cl, Cl-Zn-Cl

Torsions: Zn-O-P-C, O-Zn-O-P, Cl-Zn-O-P

Hydrogen Bonding: Cutoff distance and cutoff angle for intact hydrogen bonds

III.A MODIFIED PARAMETERS FOR EQUILIBRIUM GEOMETRIES

For the default equilibrium geometries which required modification, initial values were obtained from the Cambridge Structure Database as earlier described in chapter 2. These were then optimized by trial and error.

III.B MODIFIED FORCE CONSTANTS

Experimental stretching force constants for Zn-Cl bond are 294.2 (kcal/mol) /Å^2 for ZnCl (49) and 383.95 (kcal/mol) /Å^2 for $ZnCl_2$ (50); default DREIDING II Zn-Cl stretching force constant is 700 (kcal/mol) /Å^2. It was decided to halve the Zn-Cl stretching force constant in order to allow more flexibility in the Zn-Cl bond, in accordance with experimental data.

Close agreement was obtained between calculated and experimental results for the angles involving the metal when the force constants for angles M-O-P and O-M-O were set to 50.0 (kcal/mol)/rad^2 and the force constants for angles O-M-Cl and Cl-M-Cl were set to 40.0 (kcal/mol)/rad^2, with the equilibrium value for angle M-O-P being 145.0^o. These values were arrived at by a systematic variation of the force constants (and associated equilibrium values) for the angles involving the metal center. The default DREIDING II force constant of 100.0 (kcal/mol)/rad^2 for these angles was just too rigid and resulted in metal-center angles which did not match well with experimental geometries.

III.C MODIFIED TORSION PARAMETERS INVOLVING THE ZINC METAL

DREIDING II force field does not have parameters for torsions involving the zinc metal. A close match of calculated to experimental values for torsion angle Zn-O-P-C was obtained when we used a third order torsion force constant of 2 kcal/mol for torsion angles Zn-O-P-C, O-Zn-O-P, and Cl-Zn-O-P, with cis conformation being of maximum energy.

III.D SOLVENT PARAMETERS

The solvent system used in all cases was that of a non-constrained grid lattice built around the metal complex and extending outwards for 9.0 Å; with a specified distance of 9.0 Å for non-bond interactions, extending the solvent system outwards for at least 9.0 Å ensured all possible non-bond interactions between atoms of the complex and of the solvent. An inner cutoff distance of 2.8 Å, corresponding roughly to the Van der Waals contact between hydrogens, was allowed between the metal complex and the solvent for all solvent types used.

Benzene and *n*-hexane were allowed an optimum grid spacing of 5.0 Å with initial grid lattice types of tetragonal for benzene and cubic for *n*-hexane. Our assignment of benzene and *n*-hexane solvent parameters was based on the following points:

(1) experimental and computation studies on liquid benzene (51) which has been determined to have an intermolecular separation distance of about 6.0 Å and a tetragonal molecular arrangement for benzene molecules in liquid benzene.

(2) lattice based modeling work on *n*-hexane solvent (52) which has often used and

recommended a grid spacing of 4.5 Å and a cubic grid lattice.

(3) estimation of the minimum separation distance between two benzene or hexane molecules 'sitting' side by side.

Default DREIDING II parameters were used for the water solvent system; these were a grid spacing and an inner cutoff distance of 2.8 Å and a diamond lattice type.

III.E HYDROGEN BOND PARAMETERS

The literature (32) suggests that the mean number of intact hydrogen bonds per water molecule at 25° C is 0.73; technical literature on BIOGRAF modeling program recommends a distance range of 3.5 Å to 4.0 Å and an angle range equivalent to 150° - 130° for creation of intact hydrogen bonds. Using a hydrogen bond cutoff distance of 3.5 Å and a hydrogen bond angle cutoff value equivalent to 150° gave the mean number of intact hydrogen bonds per water molecule in the range of 0.5 to 0.7 for most systems; however, the number of intact hydrogen bonds increased after minimization, sometimes by as much as twice the initial number of intact hydrogen bonds. Using a cutoff distance of less than 3.5 Å and a cutoff angles less than 150° resulted in no intact hydrogen bonds being formed for some systems; a cutoff angle less than 130° (with cutoff distance fixed at 3.5 Å) tremendously increased the number of intact hydrogen bonds. Considering that the number of intact hydrogen bonds in a real system is very variable depending on the environmental conditions, we first decided to use the hydrogen bond cutoff distance of 3.5 Å and a hydrogen bond cutoff angle equivalent to 150° for all water-complex systems as per within the recommended range; these cutoff

values did give a reasonable number of intact hydrogen bonds that allowed evaluation of hydrogen bond effects.

A cutoff value of 3.5 Å and a cutoff angle equivalent to 140° for hydrogen bond energy calculations during minimization gave zero hydrogen bond energy in the minimized solvent-complex system when we checked the energy of the complex with consideration of the complex-solvent interactions. In contrast, the same calculations recorded some hydrogen bond energy when default DREIDING II hydrogen bond energy parameters were used in which the cutoff distance was 5.0 Å and the cutoff angle was 90°; this hydrogen bond energy decreased as the cutoff distance decreased from 5.0 Å and the cutoff angle increased from 90°. It was therefore decided to use default DREIDING II hydrogen bond energy parameters in order to observe reasonable hydrogen bond energy effects.

III.F CHARGES

'Q Equil' charge calculation program (29) had parameters for metal atoms while the other charge calculation programs on BIOGRAF (Gasteiger (30) and Del Re (31)) had no parameters for metal atoms. However, 'Q Equil' could not calculate charges for the many atoms (500 - 2000) in the solvent system while 'Gasteiger' easily calculated charges even when the number of atoms involved was large. Hence 'Q Equil' was used to calculate charges for the metal complex while the charges for the solvent system were calculated using the 'Gasteiger' program.

III.G PARAMETER SETS

Parameters developed so far, together with the default DREIDING II parameters not changed, were the ones which were used in our molecular mechanics calculations; these parameters are summarised in Table 3.2 for the triphenylphosphine oxide zinc complex. The parameters for the trialkylphosphine oxide zinc complex were identical except the C-C and C-H distances were taken as 1.530 Å and 1.090 Å respectively, and the HCP, CCP HCH, HCC and CCC angles were taken as 109.5^{0}. A figurative presentation of the charges calculated for the unsolvated complexes are given in Appendix II; these charges are similar to those calculated in the presence of the solvents.

Table 3.2: Parameter Set For Triphenylphosphine Oxide Zinc Complexes

NOTE:

Charges calculated by 'Q Equil' for complex and by 'Gasteiger' for solvent
max ------> Cis_maximum
min ------> Cis_minimum

K_r [(kcal/mol)/Å^2)], [r_o (Å)]						
	P-O	P-C	C-C	C-H	Zn-O	Zn-Cl
r_o	1.505	1.815	1.390	1.020	1.970	2.200
k_r	700	700	700	1050	700	350

K_θ [(kcal/mol)/rad^2]											
	OPC	CPC	HCP	CCP	HCH	HCC	CCC	ZnOP	OZnO	OZnCl	ClZnCl
θ_o	111.5	108.5	120.0	120.0	120.0	120.0	120.0	145.0	109.5	109.5	109.5
k_θ	100	100	100	100	100	100	100	50	50	40	40

K_ϕ [kcal/mol]												
	OPCH	OPCC	PCCH	PCCC	CPCH	CPCC	CCCC	HCCC	HCCH	OZnOP	ZnOPC	ClZnOP
k_ϕ V_2			25 (min)	25 (min)			25 (min)	25 (min)	25 (min)			
k_ϕ V_3	2 (max)	V_6=1 (min)			2 (max)	V_6=1 (min)				2 (max)	2 (max)	2 (max)

VDW[r_o (Å), ε_o [kcal/mol]						
	O	P	C	H	Zn	Cl
r_o	3.405	4.150	3.898	3.195	4.540	3.950
ε_o	0.096	0.320	0.095	0.015	0.055	0.283

IV. MINIMIZATION AND RUN PROCEDURES

A combination of steepest -descents and conjugate-gradient minimization methods was employed in minimizing the complex-solvent system. In all minimizations, the convergence criteria used were a root mean square value (rms) of 0.1 for the forces on atoms and a minimum energy change (E) between consecutive minimization steps of 0.001 kcal/mol. In each minimization, the structures were allowed to minimize up to the convergence criteria with no interruptions prior to convergence.

For better accuracy, the charges of the minimized solvent-complex system were updated and the system re-minimized; the process of charge update and re-minimization was repeated a number of times until the energy of the system was constant from one repeat process to the next.

The unsolvated ligands of the complexes were also minimized by the same minimization and run procedure as described above.

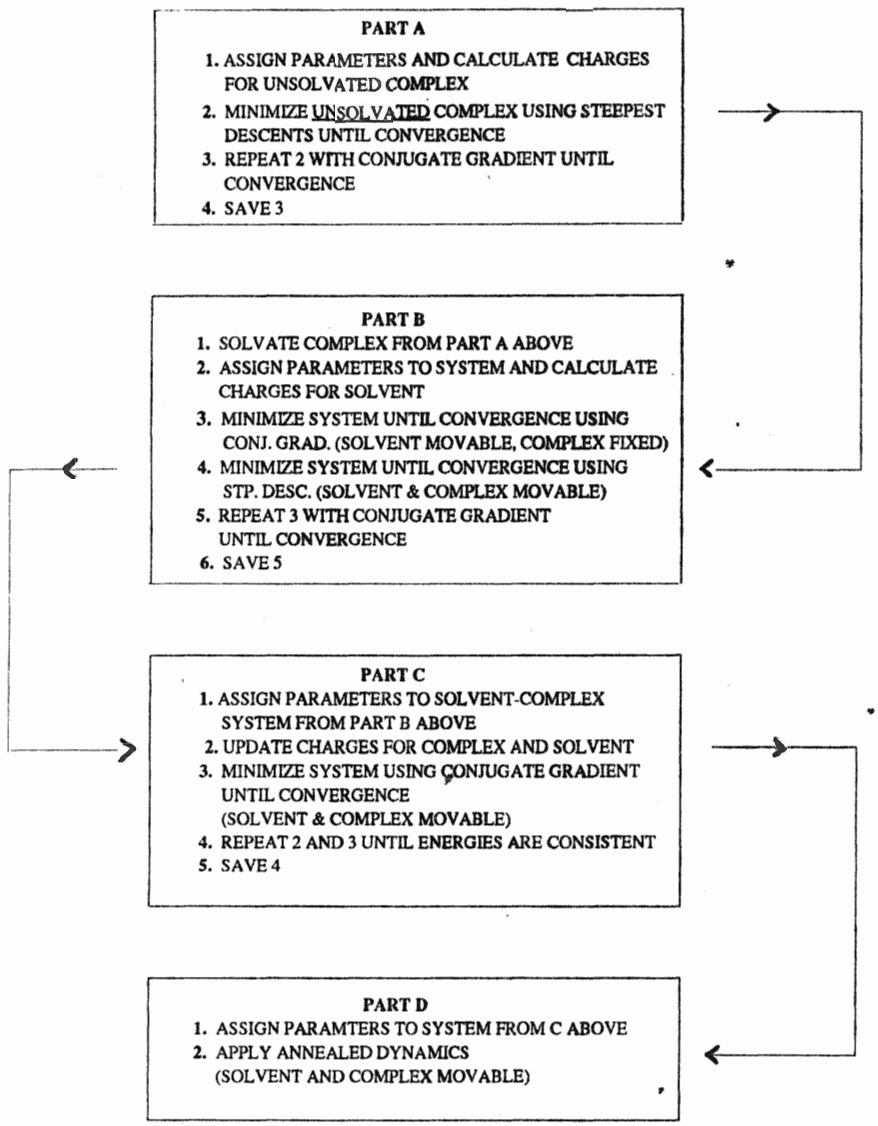
Searches for lower energy conformations were performed on the final minimized solvated systems using annealed dynamics (39) with standard Verlet dynamics algorithm (42). The dynamics temperature was varied from 300K to 600K and then back to 300K (1 cycle) at the rate of 10K every 0.1ps; dynamics calculations were done every 0.001ps. Full conjugate-gradient minimization to convergence criteria of rms=0.1 and E=0.001 was performed on the lowest energy solvent-complex system from the annealing dynamics cycle.

The flow diagram in Figure 3.1 summarises the details of the minimization procedures and run techniques:

Figure 3.1: Flow Diagram For The Minimization And Run Procedures

Terminology

'Movable' and 'Fixed' : BIOGRAF allows for defined substructures to minimize, i.e. to 'move', while the rest of the structure remains fixed; thus the solvent configuration may be minimized separately or together with the complex.



A re-run was done on the complex-solvent systems in which the complex ligand types were TMPO,TEPO, TNPPO,TBPO and TPPO to check the reproducibility of the calculated results. The same re-run was also done for the unsolvated complexes. As analyzed in the discussion chapter that follow, the results from the two trials agreed well for both the complex-solvent system and the unsolvated complexes.

4. RESULTS AND DISCUSSION

I. OVERVIEW

During solvent extraction, the solute is distributed between two essentially immiscible liquids. How much of the starting solute is present in each of the liquid phases at equilibrium is primarily determined by the following factors:

i) Solvent-solute interactions

ii) Steric energy of the solute molecule in the solvent

iii) pH of the solutions

iv) Temperature

v) Presence of other substances (modifiers) in the solutions

We employed a molecular mechanics approach to investigate the effects of solvent-solute interactions and complex steric energy on the distribution of the complex molecules between two immiscible liquids. This approach involved modeling of single metal complex solutes in pure single solvents. The calculated solvent-complex interactions and steric energies of the complexes were then used to evaluate the experimental and expected distribution ratios of metal complex molecules between two immiscible liquids. It is hoped that an understanding of solvent extraction based on solvent-solute interactions and complex steric energies in the solvents will then help in determining how the other variables listed above (iii to v) may be optimized in order to achieve better extraction.

Energy variations, with explicit treatment of the solvent, will first be discussed. This will then be followed by an attempt to estimate the distribution coefficient of the complex molecules between the organic and aqueous phases. A look at the energy accompanying the formation of the complex will be taken up in the closing section of the discussion.

Solvation effects are investigated by comparing the energy of the minimized complex with inclusion of solvent interactions to the minimized energy of the complex without inclusion of solvent interactions. To 'look' at the energy of the minimized complex with inclusion of solvent interactions, the molecular mechanics energy equation was set up in such a way that the atoms of the complex are 'movable' while those of the solvent are 'fixed'; the energy of the minimized solvent-complex system was then calculated (not minimized) using the 'one energy' function on BIOGRAF modeling program. In this way, solvent-complex interaction energy is part of the calculated total energy of the complex but the energy of the solvent molecules is not included in the calculated energy. Similarly, to 'look' at the minimized energy of the complex without inclusion of solvent interactions, the molecular mechanics energy equation was set up in such a way that the atoms of the complex are 'movable' while those of the solvent are neglected completely (that is neither 'movable' nor 'fixed' status in the force field equation); in this way, the solvent is entirely excluded from contributing to the total energy of the system when the 'one energy' function is applied.

We start with a preliminary evaluation of the calculated energies and geometries that are to be used in the discussion.

II. DATA EVALUATION

II.A REPRODUCIBILITY OF CALCULATED RESULTS

Since the potential energy surface contains many local minima (see introduction), reproducibility trials were carried out in order to test the consistency in the minimization procedures. Two trials are insufficient to explore the whole energy surface, but the general agreement of the results for all cases tried suggest that the energies and geometries obtained are representative of the system.

We obtained excellent reproducibility in the repeat runs on unsolvated zinc complexes of TMPO, TEPO, TNPPO, TBPO and TPPO. Tables 4.1 and 4.2 show some energy and geometry results from the two trials on these complexes; reproducibility in the geometries is given for one ligand only since the geometry reproducibility in the two ligands of the same complex is almost the same.

Table 4.1: Trial 1 Versus Trial 2 Calculated Energies For Unsolvated Tetrahedral $ZnCl_2L_2$ Complexes

(L = Tri-alkyl or Tri-phenyl Phosphine Oxide Ligand)

	LIGAND TYPES AND ENERGIES (energies in kcal/mole)									
TRIAL No. →	1	2	1	2	1	2	1	2	1	2
	TMPO		TEPO		TNPPO		TBPO		TPPO	
ENERGY ↓										
TOTAL	-53.0	-53.0	15.4	15.5	37.5	37.5	36.7	41.6	68.9	68.9
VDW	-5.0	-5.0	-2.9	-2.9	4.4	4.4	12.6	12.6	53.5	53.5
ELECT.	-48.8	-48.8	7.1	7.2	10.0	10.0	1.2	1.0	-6.2	-6.2
BONDS	0.1	0.1	1.2	1.2	2.8	2.8	4.1	4.3	7.4	7.4
ANGLES	0.5	0.5	6.6	6.6	14.3	14.3	13.4	13.1	8.7	8.7
TORSIONS	0.2	0.2	3.4	3.4	6.0	6.0	5.4	10.7	5.4	5.4

Table 4.2: Trial 1 Versus Trial 2 Calculated Geometries For Unsolvated Tetrahedral $ZnCl_2L_2$ Complexes

(L = Tri-alkyl or Tri-phenyl Phosphine Oxide Ligand)

	LIGANDS, DISTANCES AND ANGLES (Distances in Å, Angles in degrees)									
TRIAL No. →	1	2	1	2	1	2	1	2	1	2
BOND PARAMETER ↓	TMPO		TEPO		TNPPO		TBPO		TPPO	
P-O	1.498	1.498	1.498	1.498	1.507	1.507	1.499	1.499	1.504	1.504
M-O	1.968	1.968	1.963	1.963	1.971	1.971	1.964	1.962	1.963	1.963
P-C	1.812	1.812	1.824	1.824	1.831	1.831	1.827	1.827	1.828	1.828
M-O-P	141.5	141.4	141.1	141.0	147.2	147.2	147.7	147.2	157.2	157.2
O-M-O	113.0	113.0	105.2	105.2	113.0	113.0	105.6	114.8	88.1	88.1
Cl-M-Cl	110.9	110.9	113.2	113.2	109.5	109.5	110.8	111.7	113.9	113.9
Cl-M-O	106.0	106.0	106.6	106.6	103.3	103.3	105.7	105.6	110.9	110.9
O-P-C	110.1	110.2	108.0	108.0	107.7	107.7	107.4	107.3	106.7	106.7
C-P-C	108.5	108.5	107.4	107.4	105.3	105.3	107.4	108.0	109.0	109.0
M-O-P-C	65.1	65.1	72.7	72.6	32.2	32.2	65.7	60.3	66.6	66.6

The reproducibility in the repeat runs on solvated systems of TMPO, TEPO, TNPPO, TBPO and TPPO zinc complexes was fairly good. Tables 4.3 and 4.4 show the energy and geometry results from these two trials; again, reproducibility in the geometries is given for one ligand only since the geometry reproducibility in the two ligands of the same complex is almost the same.

Total energies were within an average precision of 3% while most of the bond and angle geometries had a precision of less than 1% (Tables 3.2 and 3.3). Torsional angles showed the biggest difference between trials 1 and 2 whereby in some cases (such as for TMPO and TBPO zinc complexes) the precision was as bad as 20%. However, the big deviation in torsional angles may be tolerated for our purpose since such deviations did not cause a significant change in the energies of the complexes; relative energies of the complexes (rather than the geometries) are the molecular properties which were most important in our calculations.

Table 4.3: Trial 1 Versus Trial 2 Calculated Energies For Solvated Tetrahedral $ZnCl_2L_2$ Complexes

(L = Tri-alkyl or Tri-phenyl Phosphine Oxide Ligand)

SOLVENT	LIGAND TYPES AND ENERGIES (energies in kcal/mole)									
	TRIAL No. →	1	2	1	2	1	2	1	2	1	2
WATER		TMPO		TEPO		TNPPO		TBPO		TPPO	
	ENERGY ↓										
	TOTAL	-129.5	-136.3	-87.9	-74.4	-74.6	-79.7	-83.3	-81.3	-22.8	-24.8
	HBONDS	-18.8	-21.3	-20.4	-9.1	-17.9	-18.4	-16.7	-22.5	-12.7	-9.3
	VDW	-13.1	-11.3	-9.8	-9.9	-2.2	-3.6	5.2	7.4	29.0	27.3
	ELECT.	-104.5	-107.8	-72.5	-66.4	-79.9	-83.6	-110.6	-104.2	-63.2	-62.7
	BONDS	0.5	0.2	1.5	1.0	3.1	3.4	3.9	4.5	6.9	6.4
	ANGLES	5.1	3.0	9.4	6.6	15.8	16.1	21.3	18.3	10.7	8.3
	TORSIONS	1.3	0.8	3.8	3.5	6.6	6.2	13.6	15.1	6.3	4.9
BENZENE		TMPO		TEPO		TNPPO		TBPO		TPPO	
	ENERGY ↓										
	TOTAL	-98.4	-95.2	-37.6	-37.6	-27.7	-27.5	-33.5	-35.4	-29.0	-28.8
	VDW	-43.9	-41.7	-49.4	-49.4	-52.3	-52.1	-53.5	-55.9	-33.8	-34.8
	ELECT.	-56.1	-54.9	0.8	0.8	1.9	1.9	-13.5	-12.7	-15.3	-14.1
	BONDS	0.2	0.2	0.9	0.9	2.4	2.5	4.0	4.1	6.7	6.9
	ANGLES	1.1	0.9	6.5	6.5	13.2	13.2	16.6	16.5	8.0	7.6
	TORSIONS	1.3	0.3	3.6	3.6	7.0	7.0	12.9	12.7	5.5	5.4
HEXANE		TMPO		TEPO		TNPPO		TBPO		TPPO	
	ENERGY ↓										
	TOTAL	-85.9	-87.3	-27.5	-25.3	-15.1	-15.1	-7.9	-8.8	3.1	-3.6
	VDW	-34.5	-35.7	-40.1	-40.7	-41.7	-41.7	-41.6	-41.3	-11.7	-12.8
	ELECT.	-52.8	-53.0	1.8	4.7	3.6	3.6	-2.9	-3.5	-7.7	-10.4
	BONDS	0.2	0.1	0.9	1.0	2.6	2.6	4.5	4.4	7.1	7.4
	ANGLES	1.0	0.9	6.1	6.0	13.8	13.8	19.1	18.4	9.4	8.5
	TORSIONS	0.3	0.4	3.8	3.7	6.6	6.6	13.0	13.2	5.8	3.7

Table 4.4: Trial 1 Versus Trial 2 Calculated Geometries For Solvated Tetrahedral $ZnCl_2L_2$ Complexes

(L = Tri-alkyl or Tri-phenyl Phosphine Oxide Ligand)

SOLVENT		LIGANDS, DISTANCES AND ANGLES (Distances in Å, Angles in degrees)									
	TRIAL No. →	1	2	1	2	1	2	1	2	1	2
WATER	BOND PARAMETER ↓	TMPO		TEPO		TNPPO		TBPO		TPPO	
	P-O	1.491	1.491	1.501	1.488	1.505	1.508	1.504	1.502	1.499	1.495
	M-O	1.952	1.971	1.965	1.961	1.973	1.972	1.965	1.963	1.960	1.960
	P-C	1.798	1.806	1.827	1.816	1.834	1.834	1.824	1.828	1.824	1.821
	M-O-P	136.1	133.8	138.0	136.0	147.0	146.5	147.1	143.7	153.4	153.5
	O-M-O	112.0	108.0	99.9	107.2	114.9	112.7	106.9	107.1	90.5	88.4
	Cl-M-Cl	123.7	110.4	118.1	110.4	102.5	102.7	109.9	105.9	128.3	118.3
	Cl-M-O	103.0	106.5	103.6	105.6	99.2	104.4	107.4	104.6	101.5	109.0
	O-P-C	107.7	106.8	108.7	106.3	107.0	106.6	103.9	104.6	107.3	106.5
	C-P-C	107.7	107.8	108.9	106.1	108.0	106.8	107.0	108.0	106.9	106.5
	M-O-P-C	84.3	65.2	72.7	69.7	36.1	42.2	111.0	82.4	64.1	69.3
BENZENE	BOND PARAMETER ↓	TMPO		TEPO		TNPPO		TBPO		TPPO	
	P-O	1.496	1.496	1.497	1.497	1.499	1.498	1.495	1.506	1.520	1.501
	M-O	1.968	1.965	1.963	1.962	1.963	1.963	1.957	1.957	1.959	1.959
	P-C	1.809	1.808	1.823	1.823	1.830	1.830	1.826	1.826	1.828	1.829
	M-O-P	140.1	138.4	139.5	139.3	146.6	146.6	146.0	146.9	156.4	156.8
	O-M-O	113.6	112.5	106.2	106.3	112.0	111.3	108.4	108.6	88.4	89.1
	Cl-M-Cl	112.2	112.2	114.9	114.6	111.8	112.1	110.0	109.6	114.7	113.2
	Cl-M-O	104.8	106.1	104.9	105.2	104.1	103.8	102.8	104.4	110.9	112.2
	O-P-C	110.0	109.5	108.5	108.5	108.0	108.1	108.5	108.7	107.1	106.9
	C-P-C	108.2	107.8	107.1	107.2	106.3	106.1	105.5	105.8	109.8	109.9
	M-O-P-C	60.4	67.9	73.8	73.4	32.6	34.0	72.3	78.6	66.9	68.6
HEXANE	BOND PARAMETER ↓	TMPO		TEPO		TNPPO		TBPO		TPPO	
	P-O	1.497	1.496	1.498	1.498	1.505	1.505	1.499	1.499	1.502	1.505
	M-O	1.967	1.968	1.963	1.961	1.967	1.967	1.963	1.962	1.960	1.963
	P-C	1.807	1.810	1.822	1.822	1.832	1.832	1.830	1.830	1.828	1.833
	M-O-P	140.2	141.1	142.7	141.2	147.4	147.4	145.6	146.4	157.9	159.3
	O-M-O	112.3	113.8	106.7	104.0	112.0	112.0	109.9	110.1	89.6	92.8
	Cl-M-Cl	110.7	111.1	108.8	109.6	111.0	111.0	109.6	110.3	114.0	112.6
	Cl-M-O	104.2	103.9	108.9	109.4	102.8	102.9	101.0	101.9	108.4	111.2
	O-P-C	110.2	110.2	107.9	108.2	108.3	108.3	108.2	107.6	105.5	105.7
	C-P-C	108.2	108.1	106.2	107.0	105.7	105.7	103.0	103.9	106.9	108.4
	M-O-P-C	63.1	67.2	65.4	69.6	35.2	35.2	76.4	83.8	67.4	73.0

II.B EXPERIMENTAL VERSUS CALCULATED GEOMETRIES

In the development of force field parameters, the unsolvated triphenylphosphine oxide (TPPO) zinc complex (44) was used as the model compound in which calculated geometries were matched to experimental geometries. As indicated in Table 4.5, the calculated and experimental geometries agree well.

Table 4.5: Experimental Versus Calculated Geometries For Tetrahedral $ZnCl_2(TPPO)_2$ Complexes

(TPPO --> Triphenylphosphine oxide ligand)

GEOMETRY BONDS	* EXPERIMENTAL (for one ligand only; same geoms for other ligand)	CALCULATED
P1-O1	1.507	1.504
P2-O2		1.505
M-O1	1.966	1.963
M-O2		1.964
P1-C1	1.764	1.828
P1-C2	1.796	1.830
P1-C3	1.825	1.833
P2-C4		1.828
P2-C5		1.833
P2-C6		1.833
ANGLES		
M-O1-P1	154.1	157.2
M-O2-P2		160.0
O1-M-O2	97.0	88.1
Cl1-M-Cl2	117.2	113.9
Cl1-M-O1	111.7	110.9
Cl1-M-O2		112.3
Cl2-M-O1	108.7	114.2
Cl2-M-O2		114.9
O1-P1-C1	109.8	106.7
O1-P1-C2	110.0	109.6
O1-P1-C3	112.9	110.5
O2-P2-C4		105.9
O2-P2-C5		109.2
O2-P2-C6		110.7
C1-P1-C2	105.1	109.0
C1-P1-C3	108.2	110.4
C2-P1-C3	110.7	110.6
C4-P2-C5		110.2
C4-P2-C6		110.4
C5-P2-C6		110.4
TORSIONS		
M-O1-P1-C1	64.5	66.6
M-O1-P1-C2	-52.6	-55.2
M-O1-P1-C3	-173.5	-175.5
M-O2-P2-C4		75.2
M-O2-P2-C5		-46.5
M-O2-P2-C6		-165.9

**Experimental geometries are as determined in reference 44*

II.C SEARCH FOR LOWER ENERGIES

Annealed dynamics was carried out on all the final minimized systems in order to search for energies lower than those obtained in the minimizations; a standard Verlet dynamics algorithm (41) was used and the temperature was varied from 300K to 600K. Except for small decreases of about 4.7% to 4.9% in the minimized energies of the water systems and 0.98% in the minimized system of trimethylphosphine oxide (TMPO) complexes in hexane, annealed dynamics did not yield systems with total energy lower than that obtained from the minimizations (Table 4.6).

Table 4.6: Minimized Versus Dynamics Total Energies For Solvent-Complex System Involving Tetrahedral $ZnCl_2L_2$ Complexes

(L = Tri-alkyl or Tri-phenyl Phosphine Oxide Ligand)

SOLVENT	* CALC TYPE	LIGAND TYPES AND ENERGIES (energies in kcal/mole)											
		STRAIGHT CHAIN						BRANCHED CHAIN					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	MIN	-2706	-2791	-3061	-3751	-5272	-6448	-2991	-3274	-3383	-3426	-5483	-3808
	DYN	-2835	-2927	-3211	-3937	-5531	-6766	-3137	-3435	-3548	-3598	-5751	-3999
	%AGE DEV	4.653	4.760	4.799	4.837	4.800	4.813	4.758	4.815	4.758	4.897	4.771	4.867
BENZENE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	MIN	134	220	279	316	436	530	258	253	254	328	380	346
	DYN	134	220	279	316	436	530	258	253	254	328	380	346
	%AGE DEV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEXANE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	MIN	41.2	125	179	185	224	260	125	137	128	223	175	197
	DYN	40.8	125	179	185	224	260	125	137	128	223	175	197
	%AGE DEV	0.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

* CALCULATION TYPE:

%AGE DEV = (|MIN - DYN|) / (AVERAGE OF MIN AND DYN)
MIN --->MINIMIZATION
DYN--->DYNAMICS

II.D CALCULATED CHARGES

It is likely that some of the charges calculated for the unsolvated complexes in Appendix II might not be correct. This is indicated by the big deviation in the charge on one of the terminal carbons on TNPPO complex relative to that on the other terminal carbons of the same complex. Further indication of errors in some charges can be seen in TNPPO and TBPO complexes where excessive positive charge occur on one or two hydrogens. These errors could be due to inefficiencies in the charge equilibriation program and measures are being taken to clarify the errors. We note, however, that such errors will not significantly affect the conclusions in our work as these errors are minor and occur in very few cases. Moreover, the errors in charges may be reproducible such that errors in the relative electrostatic energies of the complexes will cancel out or, at least, be reduced to a minimum. Problems with molecular mechanics electrostatic calculations have been known for sometime now and these are discussed more fully in reference '5'.

II.E INTRODUCTION TO DATA ANALYSIS

Having evaluated the results, the rest of this chapter will be devoted to the analysis of the calculated results in relation to the chemistry of solvent extraction.

III. STERIC ENERGY VARIATIONS

III.A STERIC ENERGY DATA

Results for the complex energies minimized in the presence of the solvents are given in Tables 4.7 and 4.8; energies in Table 4.7 take into account the solvent-complex interactions while those in Table 4.8 do not include the solvent-complex interactions (see page 61 for an explanation of how to include or exclude solvent-complex interaction in the minimized energies). Energies of the complexes and ligands which were minimized in the absence of the solvent are given in Tables 4.9 and 4.10. The associated geometries for the complexes minimized in the presence of the solvents, as well as those for the complexes minimized in the absence of the solvents, are given in Tables I.1 to I.12 in Appendix I.

Table 4.7 Steric Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes Minimized In The Presence Of The Solvent

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

*** Solvent-Complex Interactions Are Part Of The Given Energies**

SOLVENT	ENERGY TERM	LIGAND TYPES AND ENERGIES (energies in kcal/mol)											
		STRIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-129.5	-87.9	-74.6	-83.3	-124.5	-149.2	-85.2	-102.0	-115.5	-42.1	-174.2	-22.8
	VDW	-13.1	-9.8	-2.2	5.2	0.6	18.7	2.9	39.8	6.5	14.2	73.2	29.0
	ELECT.	-104.5	-72.5	-79.9	-110.6	-136.0	-183.2	-103.5	-136.8	-153.5	-88.3	-290.6	-63.2
	HBONDS	-18.8	-20.4	-17.9	-16.7	-10.5	-15.6	-11.9	-10.9	-0.8	-2.3	-30.1	-12.7
	BONDS	0.5	1.5	3.1	3.9	4.4	6.4	5.8	20.2	4.3	6.7	14.9	6.9
	ANGLES	5.1	9.4	15.8	21.3	11.1	14.9	15.9	28.8	18.6	18.1	43.3	10.7
	TORSIONS	1.3	3.8	6.6	13.6	5.9	9.6	5.6	6.9	9.5	9.5	15.1	6.3
BENZENE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-98.4	-37.6	-27.7	-33.5	-57.5	-63.2	-46.7	-59.5	-84.2	-3.5	-114.3	-29.0
	VDW	-43.9	-49.4	-52.3	-53.5	-58.5	-64.0	-41.1	-3.0	-42.3	-33.4	-14.5	-33.8
	ELECT.	-56.1	0.8	1.9	-13.5	-17.3	-23.2	-28.9	-108.7	-74.0	-3.2	-164.6	-15.3
	BONDS	0.2	0.9	2.4	4.0	4.4	6.2	4.3	19.2	4.6	7.9	15.6	6.7
	ANGLES	1.1	6.5	13.2	16.6	9.8	11.8	14.9	27.4	18.1	17.4	36.2	8.0
	TORSIONS	0.4	3.6	7.0	12.9	4.0	6.1	4.1	5.6	9.4	7.9	13.0	5.5
HEXANE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-85.9	-27.5	-15.1	-7.9	-37.2	-32.7	-30.7	-40.9	-66.9	15.2	-91.1	3.1
	VDW	-34.5	-40.1	-41.7	-41.6	-45.0	-48.6	-31.2	11.0	-29.3	-21.6	-8.1	-11.7
	ELECT.	-52.8	1.8	3.6	-2.9	-11.7	-8.5	-23.1	-102.6	-70.2	3.7	-147.5	-7.7
	BONDS	0.2	0.9	2.6	4.5	4.9	7.2	4.5	18.3	4.8	8.3	16.0	7.1
	ANGLES	1.0	6.1	13.8	19.1	10.2	11.4	14.8	26.9	18.1	16.8	36.9	9.4
	TORSIONS	0.3	3.8	6.6	13.0	4.4	5.8	4.3	5.5	9.8	8.1	11.7	5.8

** the method used in including the solvent-complex interactions is explained on page 61*

Table 4.8: Steric Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes Minimized In The Presence Of The Solvent

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

*** Solvent-Complex Interactions Are Not Part Of The Given Energies**

SOLVENT	ENERGY TERM	LIGAND TYPES AND ENERGIES (energies in kcal/mol)											
		STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-48.6	19.8	43.2	60.4	63.8	100.1	26.4	18.2	-1.2	76.6	31.6	74.7
	VDW	-4.3	-0.6	7.1	19.0	34.7	60.7	16.3	58.9	27.1	32.3	93.9	54.5
	ELECT.	-51.2	5.7	10.7	2.6	7.7	8.4	-17.2	-96.5	-60.6	9.9	-135.6	-3.9
	HBONDS	------	------	------	------	------	------	------	------	------	------	------	------
	BONDS	0.5	1.5	3.1	3.9	4.4	6.4	5.8	20.2	4.3	6.7	14.9	6.9
	ANGLES	5.1	9.4	15.8	21.3	11.1	14.9	15.9	28.8	18.6	18.1	43.3	10.7
	TORSIONS	1.3	3.8	6.6	13.6	5.9	9.6	5.6	6.9	9.5	9.5	15.1	6.3
BENZENE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-52.8	16.1	40.2	53.3	53.2	84.0	20.6	12.8	-6.3	70.2	1.2	69.4
	VDW	-4.6	-2.1	5.8	17.0	32.1	52.6	-14.0	57.3	23.5	27.1	80.4	55.2
	ELECT.	-49.8	7.2	11.8	2.8	2.9	7.4	-16.7	-96.7	-61.9	10.0	-144.0	-5.9
	BONDS	0.2	0.9	2.4	4.0	4.4	6.2	4.3	19.2	4.6	7.9	15.6	6.7
	ANGLES	1.1	6.5	13.2	16.6	9.8	11.8	14.9	27.4	18.1	17.4	36.2	8.0
	TORSIONS	0.4	3.6	7.0	12.9	4.0	6.1	4.1	5.6	9.4	7.9	13.0	5.5
HEXANE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-53.1	16.5	39.9	58.7	53.4	81.6	19.0	13.2	-6.0	70.2	8.5	71.8
	VDW	-4.6	-1.9	5.9	16.8	30.7	52.0	13.3	58.2	23.0	26.0	82.1	54.2
	ELECT.	-50.0	7.6	11.0	5.4	3.2	5.3	-18.0	-95.8	-61.7	11.0	-138.2	-4.9
	BONDS	0.2	0.9	2.6	4.5	4.9	7.2	4.5	18.3	4.8	8.3	16.0	7.1
	ANGLES	1.0	6.1	13.8	19.1	10.2	11.4	14.8	26.9	18.1	16.8	36.9	9.4
	TORSIONS	0.3	3.8	6.6	13.0	4.4	5.8	4.3	5.5	9.8	.8.1	11.7	5.8

** the method used in excluding the solvent-complex interactions is explained on page 61*

Table 4.9: Steric Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes Minimized In The Absence Of The Solvent

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

ENERGY TERM	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
	STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
	TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
TOTAL	-53.0	15.4	37.5	36.7	50.6	74.5	18.7	12.1	-6.7	68.8	-1.3	68.9
VDW	-5.0	-2.9	4.4	12.6	30.5	47.2	13.0	55.8	20.8	25.1	75.7	53.5
ELECT.	-48.8	7.1	10.0	1.2	2.4	3.6	-18.1	-96.5	-59.6	10.1	-141.0	-6.2
BONDS	0.1	1.2	2.8	4.1	5.2	8.3	4.8	19.5	5.2	8.7	16.9	7.4
ANGLES	0.5	6.6	14.3	13.4	9.1	10.8	14.8	27.7	17.8	17.0	36.0	8.7
TORSIONS	0.2	3.4	6.0	5.4	3.4	4.6	4.2	5.6	9.0	7.9	11.0	5.4

Table 4.10: Steric Energy Data For Phosphine Oxide Ligands Minimized In The Absence Of The Solvent

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

ENERGY TERM	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
	STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
	TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
TOTAL	-21.2	10.7	24.1	31.6	32.6	46.4	18.5	18.1	6.6	41.6	-3.2	41.0
VDW	-0.5	1.9	6.1	9.6	18.7	29.4	10.4	30.5	15.0	14.0	40.8	32.3
ELECT.	-20.9	6.5	8.5	6.0	6.3	8.0	-1.0	-35.1	-23.5	15.5	-68.5	3.3
BONDS	0.0	0.4	1.4	2.2	3.0	3.8	2.2	9.2	2.7	3.7	7.7	3.9
ANGLES	0.1	1.9	6.2	10.1	4.0	4.4	5.1	11.7	10.2	6.1	11.3	1.4
TORSIONS	0.0	0.1	1.9	3.6	0.4	0.8	1.8	1.8	2.2	2.3	5.5	0.1

III.B SOLVATION ENERGY DATA

Calculated solvent-complex interaction energies ($E_{solvatn}$) for the modeled metal complexes in water, benzene and hexane are given in Table 4.11. Solvent-complex interaction energies ($E_{solvatn}$) were calculated by subtracting the sum of the total energies for the complex and the solvent ($E_{cpx} + E_{solv}$) from the total energy of the solvent-complex system ($E_{solv+cpx}$).

That is,

$$E_{solvatn} = E_{solv + cpx} - (E_{solv} + E_{cpx})$$

A further break-down of the solvent-complex interaction energy into its electrostatic ($E_{solvatn}$[elect.]), Van der Waals ($E_{solvatn}$[vdw]) and hydrogen bond ($E_{solvatn}$[hbnd]) components is also included in Table 4.11; solvent-complex interaction energy components were calculated from Tables 4.7 and 4.8 whereby the solvation energy components are the changes in electrostatic, Van der Waals and hydrogen bond energy terms that occur when the energy of the complex is calculated with and without consideration of the solvent-complex interactions.

Table 4.11: Calculated Solvation Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes
(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

SOLVNT	ENERGY TERM	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
		STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	$E_{solvatn}$	-80.9	-107.7	-117.8	-143.8	-188.4	-249.3	-111.6	-120.2	-114.4	-118.7	-205.8	-97.5
	$E_{solvatn}$(elect.)	-53.3	-78.1	-90.6	-113.2	-143.6	-191.6	-86.3	-90.3	-92.9	-98.2	-155.0	-59.3
	$E_{solvatn}$(vdw)	-8.8	-9.2	-9.3	-13.9	-34.2	-42.0	-13.4	-19.1	-20.6	-18.1	-20.7	-25.5
	$E_{solvatn}$(hbnd)	-18.8	-20.4	-17.9	-16.7	-10.5	-15.6	-11.9	-10.9	-0.8	-2.3	-30.1	-12.7
BENZN		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	$E_{solvatn}$	-45.6	-53.7	-67.9	-86.7	-110.7	-147.2	-67.3	-72.4	-77.9	-73.6	-115.5	-98.4
	$E_{solvatn}$(elect.)	-6.3	-6.4	-9.9	-16.3	-20.1	-30.6	-12.2	-12.0	-12.1	-13.2	-20.6	-9.4
	$E_{solvatn}$(vdw)	-39.3	-47.3	-58.1	-70.5	-90.6	-116.6	-55.1	-60.3	-65.8	-60.5	-94.9	-89.0
HEXAN		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	$E_{solvatn}$	-32.7	-43.9	-54.9	-66.7	-90.6	-114.3	-49.7	-54.0	-60.9	-55.0	-99.6	-68.6
	$E_{solvatn}$(elect.)	-2.8	-5.8	-7.4	-8.3	-14.9	-13.8	-5.1	-6.8	-8.5	-7.3	-9.3	-2.8
	$E_{solvatn}$(vdw)	-29.9	-38.2	-47.6	-58.4	-75.8	-100.6	-44.5	-47.2	-52.3	-47.6	-90.3	-65.9

III.C RELATIVE STERIC ENERGIES FOR ZINC COMPLEXES IN WATER, BENZENE AND HEXANE

For the steric energies in which solvent interactions are included (Table 4.7), the data show that the steric energy of complexes in water is more favourable than that of complexes in benzene and hexane, with complexes in hexane showing the least favourable steric energies. This can be attributed to the solvation effects as indicated in Table 4.11 whereby zinc complexes in water are better solvated than zinc complexes in either benzene or hexane, with the zinc complexes in hexane being the least solvated.The better electrostatic solvation interactions for the water system, together with an additional favourable hydrogen bond solvation energy (Table 4.11), leads to better solvation effects for complexes in water than for those in benzene and hexane. Though the Van der Waals solvation energies for complexes in benzene and hexane are more favourable than Van der Waals solvation energies for complexes in water (Table 4.11), the Van der Waals solvation energies for complexes in benzene and hexane are not as favourable as the combined solvation energy due to electrostatics and hydrogen bonding for the complexes in water; as such, water solvated complexes still show more favourable solvation and steric energies than complexes in benzene and hexane.

Contrary to experimental observation (1, 53), the more favourable calculated steric energy for complexes in water relative to complexes in benzene and hexane would predict that phosphine oxide zinc complexes are not well extracted into the organic solvents. This

contradiction of experimental facts could be due to suspected errors in the calculated charges. As discussed later (pages 100 to 105), calculations without inclusion of charges show that the relative steric energies in the simulated water and organic phases will allow reasonable extraction into the organic phase. We further note that our calculations did not include the entropy of the system which would otherwise reveal more information about the relative stabilities of the complexes in the solvents.

The better solvation of zinc complexes in benzene relative to zinc complexes in hexane is due to better electrostatic and Van der Waals solvation interactions in benzene compared to the case where the complexes are in hexane (Table 4.11). If we assume a direct correlation between solvation energy and solubility, the better solvation in benzene systems relative to hexane systems would be in agreement with the experimental observation on CYANEX 921 whereby the solubility of CYANEX 921 is higher in the aromatic diluents than in aliphatic diluents (1).

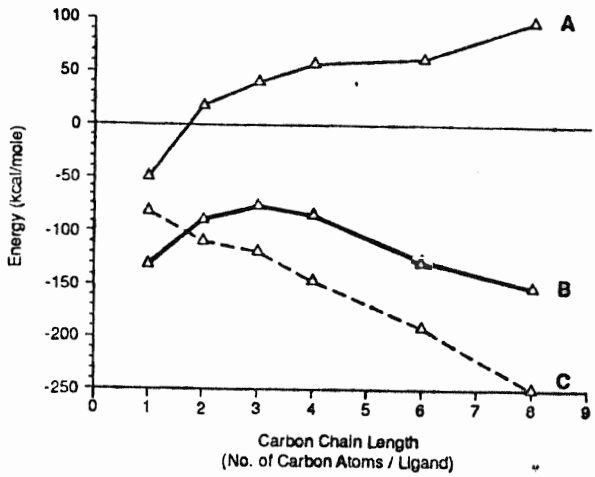
III.D STERIC ENERGY VARIATIONS WITH CHANGE IN LIGAND CARBON CHAIN LENGTH

Figure 4.1 on the following page show different plots of steric and solvation energies associated with complexes of increasing ligand carbon chain length; the plotted steric energy data comes from Tables 4.7 and 4.8 while the complex solvation energy data is obtained from Table 4.11.

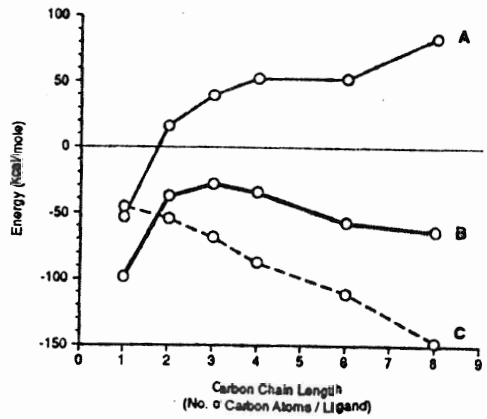
Figure 4.1: Plots Of Steric Energy Against Carbon Chain Length For Tetrahedral $ZnCl_2L_2$ Complexes In (I) Water (II) Benzene And (III) *n*-Hexane
(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

A = Steric Energy Without Solvent Interactions; *B = Steric Energy With Solvent Interactions;*
C = Solvation Energy;

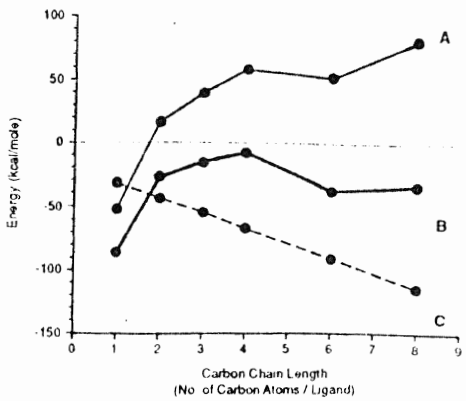
(I) WATER SYSTEM:



(II) BENZENE SYSTEM:



(III) HEXANE SYSTEM:



If steric energy is calculated without inclusion of solvent interactions, the data shows that the total energies of the complexes increase as the carbon chain length increases (Figure 4.1, graph A); this trend has also been observed elsewhere (17). On the other hand, when solvation interactions are included in the calculations, the data shows that the steric energy increases only up to carbon chain length three or four, after which the steric energy starts dropping (Figure 4.1, graph B). The effects in graph B, as opposed to those in graph A, can be attributed to solvation effects plotted in graph C of Figure 4.1. This is to say that as the carbon chain length increases, a balance between increasing steric energy of the isolated complex (graph A) and decreasing solvation energy of the solvated complex (graph C) gives the steric energy of the solvated complex (graph B); how much a drop in energy due to solvent-complex interactions (graph C) relative to how much a rise in energy due to increase in total energy of the isolated complex (graph A) will determine the solvent stabilization effects.

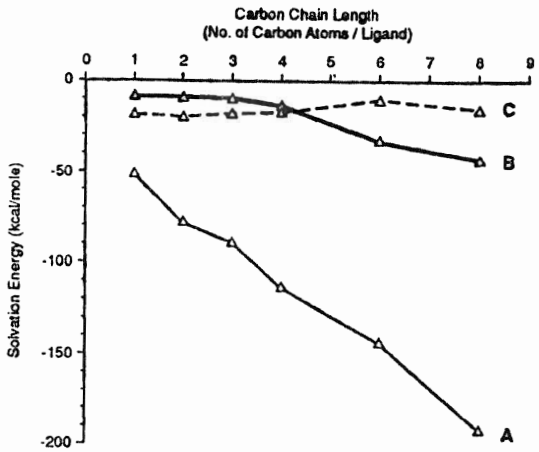
Since electrostatic, Van der Waals and hydrogen bonding energies are the only energy terms that vary upon solvation of a given complex, differences in the nature of the drop in solvation and steric energy with increase in carbon chain length for the solvated complex may be attributed to the way these interactions vary as the carbon chain length increases. This is illustrated graphically in Figure 4.2 on the following page in which solvation energy components in Table 4.11 are plotted against carbon chain length for the water, benzene and hexane systems:

Figure 4.2: Plots Of Solvation Energy Components Against Ligand Carbon Chain Length For Tetrahedral $ZnCl_2L_2$ Complexes In (I) Water (II) Benzene And (III) *n*-Hexane

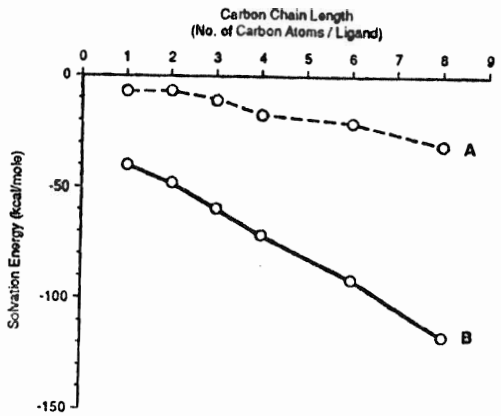
(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

A = Electrostatics; *B = Van der Waals;* *C = Hydrogen Bonding;*

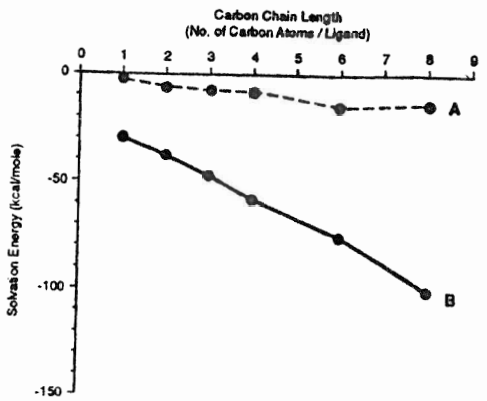
(I) WATER SYSTEM:



(II) BENZENE SYSTEM:



(III) HEXANE SYSTEM:



For water solvated complexes, the drop in electrostatic solvation energy with increase in carbon chain length is greater than the drop in Van der Waals interactions with increase in carbon chain length (Figure 4.2, part I); in contrast, benzene and hexane show a steeper curve for Van der Waals interactions than for electrostatic interactions as the carbon chain length increases (Figure 4.2, parts II and III). What these observations indicate is that electrostatic interactions are more important than Van der Waals interactions in changing the water-complex solvation interactions as the carbon chain length increases while Van der Waals interactions (as opposed to electrostatic interactions) are more important in changing the benzene-complex or hexane-complex interactions as the carbon chain length increases.

For the purpose of solvent extraction, the relationship between graphs A and B of Figure 4.1 as explained in this section does illustrate the important concept that steric effects due to increasing carbon chain length can be overcome by appropriate adjustment of the electrostatic and Van der Waals interactions. Thus, for straight chain ligands, one way of modifying the electrostatic interactions will be to adjust the pH of the aqueous phase while Van der Waals interactions may be varied by changing the solvent type or ligand carbon chain length; addition of a modifier (such as chloride ions) to the effluent, will also affect the electrostatic interactions in the solvent extraction system.

III.E COMPLEX STERIC ENERGIES OF STRAIGHT CHAIN LIGANDS VERSUS THAT OF BRANCHED CHAIN LIGANDS

In both cases where the steric energy of the complex is calculated with and without

inclusion of solvent interactions (Tables 4.7 and 4.8), comparison of total steric energies for complexes involving tri-*n*-butylphosphine oxide (TBPO) to that of complexes involving the branched forms of tri-*tert*-butylphosphine oxide (TTPO) and tri-*iso*-butylphosphine oxide (TIPO) show a decrease in total steric energy upon branching; a similar decrease in total steric energy for the zinc complexes is observed when tri-*n*-propylphosphine oxide (TNPPO) is branched to tri-*sec*-propyphosphine oxide (TSPPO) or when tri-*n*-octylphosphine oxide (TOPO) is branched to trimethylpentyl-*n*-octylphosphine oxide (TPOPO).

Generally speaking, the more favourable electrostatic energies in branched ligand systems (as indicated by the electrostatic energies of isolated complexes with branched chain ligands in Tables 4.8 and 4.9) account for most of the favourable energy upon branching of the ligand. Comparison of charges calculated by the 'Charge Equilibration' program (29) for the branched chain ligands to those calculated by the same program for the straight chain ligands (Appendix II) show that complexes with branched ligands have a more favourable charge distribution than complexes of straight chain ligands. The favourable charge distribution as stated here may be understood by considering the electrostatic potential function as used in molecular mechanics whereby the electrostatic energy is directly related to the product of the interacting charges and inversely related to the distance between the charges; in other words, a favourable electrostatic energy arises where large charges with a large charge difference are close to one another. Therefore, for the branched ligand systems where the carbon at the branching point is more electropositive and the methyl carbon is

more electronegative (e.g., TTPO case), a favourable electrostatic potential is expected as long as the interacting opposite charges are close enough. On the other hand, for straight chain systems where methylene carbons are less electronegative and the more electronegative methyl carbons are fewer in number (e.g., the TBPO case), the electrostatic potential energy is likely to be less favourable. Hence, since increased branching of the hydrocarbon chain results in more branching point and methyl carbons, we can generally say that a branched ligand system will lead to a more favourable electrostatic potential than is the case in a similar straight chain ligand system. Of course the overall electrostatic potential will depend on the overall charge distribution in the system. Due to the many electrostatic interactions in the system, the scope of our project does not allow us to precisely define a favourable charge distribution for a favourable electrostatic energy. However, it appears from our data (electrostatic energy in Table 4.8 and the associated charges in Appendix II) that a favorable charge distribution is one in which charges, with large charge differences, are present in the same system (e.g., the TTPO case).

From the preceeding discussion in this section, we can see that increased steric crowding accompanying branching of a straight chain ligand is counteracted by better electrostatic energy. This observation paralles the electronic inductive effects of related phosphonates as predicted by Preston and du Preez (53); Preston and du Preez predict that on the basis of the electronic effect of the substituent groups, the extractant strength would be expected to increase in the order of *n*-butyl < *iso*-butyl < *sec*-butyl < *tert*-butyl, whereas on

the basis of the steric crowding of these groups, the reverse order would be expected.

Tables 4.7 and 4.8 show that there is a significant increase in bond strain energies of about 16 kcal/mol for complexes of tri-*tert*-butylphosphine oxide (TTPO) when compared to complexes of tri-*n*-butylphosphine oxide (TBPO). Increased bond energy in TTPO complexes is brought about by a big deviation in P-C bond distances from the equilibrium value of 1.805 Å to an average value of 1.890 Å in the minimized TTPO complexes (Table I.8, in Appendix I). The increased steric effects in TTPO complexes brought about by branching of the TBPO complex (as indicated in Table 4.8 by the steric energies of the complexes without solvent interactions) could be the reason for the observed long P-C distances whereby the ligands try to 'spread out' in order to counter the effects of increased steric effects. We note in this case that the steric energy of the solvated branched chain TTPO complexes still remains more favourable than that of the solvated straight chain TBPO complexes. This is because the increase in steric energy involved, when the TBPO complex is branched to the TTPO complex (as indicated by the isolated TBPO and TTPO complexes in Table 4.8), is not big enough to offset the gain in electrostatic solvation energy involved when the solvated TBPO complex is branched to the TTPO complex (as indicated by the solvation energy data for TBPO versus TTPO complexes in Table 4.11); as such, there is an overall drop in the total steric energy of the solvated complex when TBPO is branched to TTPO.

An exception to the steric energy trend observed upon branching of the solvated

complex is seen in the comparison of the steric energy with solvent interactions for zinc complexes involving tri-*n*-butylphosphine oxide (TBPO) to the steric energy of solvated complexes involving tri-*sec*-butylphosphine oxide (TSBPO) whereby an increase (instead of a decrease) in the steric energy of the solvated complex is observed on branching from TBPO to TSBPO for all three solvent systems (Table 4.7). This increased steric energy in the branched TSBPO complexes is mainly due to the fact that TSBPO ligands themselves have a relatively unfavourable steric energy as indicated in Table 4.10. The calculated individual steric energy terms in Table 4.10 show that the unexpected increase in steric energy associated with branching from TBPO to TSBPO come from the unfavourable non-bond steric energy in the ligand itself; this is to say that, unlike in the other trialkylphosphine oxide ligands where an unfavourable positive Van der Waals energy is accompanied by a favourable negative electrostatic energy, TSBPO show unfavourable positive energies for both the electrostatic and Van der Waals non-bond energy terms. This leads to the observed unfavourable non-bond energy in the TSBPO ligand. Calculated charges for TSBPO (Appendix II) show that the charge distribution in TSBPO is not as favourable as in the other branched systems; this could be part of the reason for the unfavourable electrostatic energy in TSBPO. This comparison of TBPO to TSBPO complexes is a testimony that exceptions to the general trend cannot be ruled out when we compare the energies of straight chain ligand systems to that of branched chain ligand systems.

III.F COMPLEX STERIC ENERGIES FOR TRIALKYL- VERSUS TRIPHENYL PHOSPHINE OXIDE LIGANDS

For both cases in which solvent interactions are included or excluded in the steric energy, there is a big increase in the total steric energy of complexes involving triphenylphos--phine oxide ligand (TPPO) relative to the total steric energy of similar trialkylphosphine oxide complexes having approximately the same number of atoms and bonds (Tables 4.7 and 4.8). As was the case in the comparison of straight chain TBPO complexes to branched chain TSBPO complexes, the increased steric energy in TPPO complexes relative to similar trialkylphosphine oxide complexes originate from the unfavourable non-bond energy (Van der Waals and electrostatic energies) in the ligand itself (Table 4.10). While the unfavourable electrostatic energy in the ligand did account for most of the unfavourable non-bond energy in the TSBPO ligands, the increased non-bond interactions in the TPPO ligands could mainly be attributed to excessive Van der Waals interactions in the ligand (Table 4.14). The high Van der Waals energy in TPPO ligand is likely to arise from the three bulky phenyl groups being confined within a limited space; confinement of phenyl groups of the ligand in a limited space is evident from the calculated geometries in which the P-C distances and C-P-C angles of ligands involving smaller alkyl groups are similar to the P-C distances and C-P-C angles of the TPPO ligand involving the bulky phenyl groups (Appendix I).

We further note from Table 4.11 that TPPO complexes are well solvated. However, the favourable solvation energy of TPPO ligands is not big enough to offset the unfavorable

steric energy in the ligands themselves such that the steric energy with solvent interactions for the TPPO complex still remain unfavourable when compared to that of trialkylphosphine oxide ligands (Table 4.7). Secondly, the wider Zn-O-P angles of TPPO complexes relative to that of trialkylphosphine oxide complexes (Appendix I) is an indication that the two bulky ligand groups in the complex try to stay away from each other so as to minimize the non-bond interactions between the two ligands in the complex; again, the energy of the complex still remains unfavourable because the ligands themselves are of high energy. Note here that the energy of the unstrained bonds is expected to be significant in this comparison of alkyl and phenyl systems because there is a significant difference in the bond types of the two systems. Therefore, at this point, we cannot make a firm conclusion on the relative steric energies of alkyl and phenyl systems until we have added the energy of the unstrained bonds to the calculated steric energies; DREIDING II force field does not calculate the energy of the unstrained bonds.

IV. SIMULATED DISTRIBUTION COEFFICIENTS

IV.A CALCULATION METHOD

Distribution coefficients for the complex molecules between two immiscible solvents can be estimated by comparing the complex solubilities in the organic and aqueous phases. The solubility of the complexes can be approximated from the Gibb's free energy associated with the dissolution of the complex in the solvents.

Two basic reaction steps may be assumed to be taking place during solvent extraction:

(1) Complex formation in aqueous phase;

$$Zn^{2+}_{(aq)} + 2Cl^{-} + 2R_3PO_{(aq)} \rightleftharpoons ZnCl_2(R_3PO)_{2\ (aq)}$$

(2) Dissolution of the complex from the aqueous into the organic phase;

$$ZnCl_2(R_3PO)_{2\ (aq)} \rightleftharpoons ZnCl_2(R_3PO)_{2\ (org)}$$

In this section, reaction '2' only will be used in estimating the distribution coefficients; the effects of complexation energy (reaction '1') on the distribution ratio is briefly discussed in appendix IV. Following below and the next two pages are the details that may be employed in estimating the distribution coefficients based on reaction '2' only:

For the system at equilibrium,

$$[C]_{aqueous} \rightleftharpoons [C]_{organic}$$

where

$[C]_{aqueous}$ = concentration of complex molecules in aqueous phase and

$[C]_{organic}$ = concentration of complex molecules in organic phase

the distribution coefficient (D), expressed in terms of concentration (C), is:

$$D = \frac{[C]_{organic}}{[C]_{aqueous}}$$

The respective concentrations in organic and aqueous phases may be approximated to solubilities in the organic and aqueous phases such that,

$$D = \frac{[C]_{organic}}{[C]_{aqueous}} \sim \frac{\text{Solubility of C in organic phase}}{\text{Solubility of C in aqueous phase}} \quad .....(4.1)$$

For the dissolution reaction,

$$(Complex)_{solid} \underset{\longleftarrow}{\xrightarrow{K}} (Complex)_{solution}$$

the Gibb's free energy (ΔG) of dissolution is:

$$\Delta G = \Delta H - T\Delta S = -2.303\ R\ T \log K \quad .....(4.2)$$

Where,

K = equilibrium constant for the conversion between the complex in solid form and the complex in solution form.

ΔH = enthalpy of formation in Joules

ΔS = entropy

T = temperature in Kelvins

R = general gas constant = 8.314 $JK^{-1}mol^{-1}$

The relative solubilities between the organic and aqueous phases, as expressed in equation 4.1 on the previous page, can be related to the associated relative Gibb's free energies (ΔG) and distribution coefficient (D) as give in equation 4.3 below:

$$\frac{\text{Solubility of C (in organic)}}{\text{Solubility of C (in aqueous)}} = \frac{K_{ORGANIC}}{K_{AQUEOUS}} = \frac{10^{-\Delta G(Organic)}/2.303RT}{10^{-\Delta G(Aqueous)}/2.303RT} = D \quad ...(4.3)$$

The following approximations may be applied to equations 4.2 and 4.3:

(1) ΔS is not calculable in molecular mechanics calculations. Therefore ΔS may be neglected in an attempt to determine whether the quantities calculated by molecular mechanics are useful predictors of solvent extraction parameters.

(2) ΔH may be considered to be made up of steric energy and bond energy increments for a strain-free molecule (54). Since bond energy increments for a given type of bond and molecule are considered to be constants, this will cancel out in the consideration of relative energies.

Applying approximation '1' and '2' above to equation 4.3, and hence substituting ΔG for the calculated steric energies, does not give reasonable values of D.

One way of estimating the relative solubilities (and hence the relative solvation energies) in aqueous and organic solvents is to take the <u>difference</u> of the steric energies in the simulated two phases such that

$$D^{*} = E(\text{Aqueous}) - E(\text{Organic}) \quad \text{.....(4.4)}$$

Where,

D^{*} is a parameter whose value simulates the distribution coefficient.

With the equation as given above (equation 4.4), a negative value of D^{*} would imply a negative potential for the movement of the solute molecules from aqueous to organic phase and hence a poor extraction into the simulated organic phase.

IV.B D* FROM DATA WITH ELECTROSTATIC ENERGY TERM

Using equation 4.4 and steric energy data in Table 4.7, we obtained the simulated distribution coefficient values (D^{*}) as indicated in Table 4.12 below:

Table 4.12: Simulated Distribution Coefficient Values (D^{*}) For Tetrahedral $ZnCl_2L_2$ Complexes With Electrostatics In The Energy Terms
(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

SYSTEM	CALC TYPE	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
		STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
BENZENE/ WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	D^{*}	-31.1	-50.3	-46.9	-49.8	-67.0	-86.0	-38.5	-42.5	-31.3	-38.6	-59.9	6.2
HEXANE/ WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	D^{*}	-43.6	-60.4	-59.5	-75.4	-87.3	-116.5	-54.5	-61.1	-48.6	-57.3	-83.1	-25.9

Though the trends may yield some chemical information about solvent extraction, the estimated distribution coefficients of negative for almost all the complexes is not a good simulation of extraction coefficients. As earlier mentioned, it appears the charges calculated by the computer algorithm on biograf are not good enough, leading to suspect calculated electrostatic energies.

To better simulate the extraction coefficients, the energies were recalculated without inclusion of electrostatic energies. The results obtained are discussed in the section that follows.

V. STERIC ENERGY WITHOUT INCLUSION OF ELECTROSTATIC ENERGIES

V.A STERIC AND SOLVATION ENERGY DATA

Results for the complex energies minimized in the presence of the solvents are given in Tables 4.13 and 4.14; energies in Table 4.13 take into account the solvent-complex interactions while those in Table 4.14 do not include the solvent-complex interactions (see page 61 for an explanation of how to include or exclude solvent-complex interaction in the minimized energies).

Calculated solvent-complex interaction energies ($E_{solvatn}$) for the modeled metal complexes in water, benzene and hexane are given in Table 4.15. Solvent-complex interaction energies ($E_{solvatn}$) were calculated as explained on page 78.

Table 4.13 Steric Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes Minimized In The Presence Of The Solvent And Without Electrostatics

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

*** Solvent-Complex Interactions Are Part Of The Given Energies**

SOLVENT	ENERGY TERM	LIGAND TYPES AND ENERGIES (energies in kcal/mol)											
		STRIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-43.8	-37.1	-18.0	-10.4	-15.3	-15.0	-12.2	61.9	11.5	10.0	54.6	82.0
	VDW	-16.3	-18.2	-18.0	-14.0	-15.0	-16.2	-8.0	26.7	-11.2	-7.7	21.7	32.3
	ELECT.	----	----	----	----	----	----	----	----	----	----	----	----
	HBONDS	-28.8	-27.9	-21.9	-26.5	-18.5	-20.0	-26.0	-17.4	-8.5	-9.1	-26.1	-23.7
	BONDS	0.0	0.6	2.0	3.3	4.4	5.8	4.1	20.4	5.3	6.5	17.4	10.7
	ANGLES	0.8	5.3	13.5	16.4	9.4	11.2	13.9	26.8	17.9	14.1	32.6	59.4
	TORSIONS	0.6	3.1	6.4	10.5	4.9	4.4	3.8	5.4	8.0	6.2	9.0	3.3
BENZENE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-43.6	-44.4	-35.9	-34.0	-64.8	-69.4	-22.2	43.0	-16.4	-17.8	24.2	52.6
	VDW	-44.6	-51.8	-57.3	-61.9	-83.6	-93.2	-44.7	-9.7	-48.4	-48.1	-35.9	-20.1
	ELECT.	----	----	----	----	----	----	----	----	----	----	----	----
	BONDS	0.0	0.6	2.0	3.3	4.2	6.3	3.9	20.5	5.4	6.7	18.2	11.0
	ANGLES	0.6	4.6	13.1	15.3	10.5	12.6	14.7	27.0	17.4	16.3	31.7	56.4
	TORSIONS	0.4	2.2	6.3	9.3	4.2	5.0	3.9	5.3	9.2	7.2	10.2	5.3
HEXANE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-34.1	-30.4	-21.7	-9.1	-32.6	-35.7	-10.4	56.9	-1.6	7.9	44.2	81.2
	VDW	-34.7	-39.4	-43.6	-43.5	-51.1	-59.7	-33.1	4.5	-33.7	-23.8	-23.9	4.9
	ELECT.	----	----	----	----	----	----	----	----	----	----	----	----
	BONDS	0.0	0.6	2.1	4.0	5.1	6.7	3.9	20.8	5.5	7.3	19.8	11.8
	ANGLES	0.4	4.5	14.1	18.5	9.4	12.4	14.5	26.3	17.3	16.3	38.4	58.4
	TORSIONS	0.2	3.8	5.7	12.0	4.0	4.9	4.4	5.4	9.3	8.2	9.9	5.9

** the method used in including the solvent-complex interactions is explained on page 61*

Table 4.14: Steric Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes Minimized In The Presence Of The Solvent And Without Electrostatics

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

*** Solvent-Complex Interactions Are Not Part Of The Given Energies**

SOLVENT	ENERGY TERM	LIGAND TYPES AND ENERGIES (energies in kcal/mol)											
		STRIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-3.8	7.4	27.1	44.8	48.2	69.6	34.5	107.0	52.2	49.5	130.3	140.4
	VDW	-5.2	-1.6	5.2	14.7	29.5	48.2	12.7	54.5	20.9	22.7	71.3	66.9
	ELECT.	----	----	----	----	----	----	----	----	----	----	----	----
	HBONDS	----	----	----	----	----	----	----	----	----	----	----	----
	BONDS	0.0	0.6	2.0	3.3	4.4	5.8	4.1	20.4	5.3	6.5	17.4	10.7
	ANGLES	0.8	5.3	13.5	16.4	9.4	11.2	13.9	26.8	17.9	14.1	32.6	59.4
	TORSIONS	0.6	3.1	6.4	10.5	4.9	4.4	3.8	5.4	8.0	6.2	9.0	3.3
BENZENE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-4.0	7.1	26.8	41.8	44.4	69.9	34.6	107.4	51.5	53.9	129.6	141.9
	VDW	-5.0	-0.3	5.4	13.9	25.5	46.1	12.1	54.6	19.5	23.7	69.5	69.2
	ELECT.	----	----	----	----	----	----	----	----	----	----	----	----
	BONDS	0.0	0.6	2.0	3.3	4.2	6.3	3.9	20.5	5.4	6.7	18.2	11.0
	ANGLES	0.6	4.6	13.1	15.3	10.5	12.6	14.7	27.0	17.4	16.3	31.7	56.4
	TORSIONS	0.4	2.2	6.3	9.3	4.2	5.0	3.9	5.3	9.2	7.2	10.2	5.3
HEXANE		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	TOTAL	-4.4	7.8	26.9	49.7	45.9	70.6	35.0	107.0	51.9	56.9	139.1	144.8
	VDW	-5.0	-1.2	5.0	15.3	27.4	46.6	12.3	54.6	19.9	25.2	71.0	68.5
	ELECT.	----	----	----	----	----	----	----	----	----	----	----	----
	BONDS	0.0	0.6	2.1	4.0	5.1	6.7	3.9	20.8	5.5	7.3	19.8	11.8
	ANGLES	0.4	4.5	14.1	18.5	9.4	12.4	14.5	26.3	17.3	16.3	38.4	58.4
	TORSIONS	0.2	3.8	5.7	12.0	4.0	4.9	4.4	5.4	9.3	8.2	9.9	5.9

** the method used in excluding the solvent-complex interactions is explained on page 61*

Table 4.15: Calculated Solvation Energy Data For Tetrahedral $ZnCl_2L_2$ Complexes Minimized Without Electrostatics

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

SOLVNT	ENERGY TERM	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
		STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	$E_{solvatn}$	-40.0	-44.5	-45.1	-55.2	-63.5	-84.4	-46.7	-45.2	-40.7	-39.5	-75.7	-58.4
	$E_{solvatn}$(vdw)	-11.1	-16.6	-23.1	-28.7	-45.0	-64.4	-20.7	-27.8	-32.1	-30.4	-49.6	-34.6
	$E_{solvatn}$(hbnd)	-28.8	-27.9	-21.9	-26.5	-18.5	-20.0	-26.0	-17.4	-8.5	-9.1	-26.1	-23.7
BENZN		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	* $E_{solvatn}$	-39.6	-51.4	-62.6	-75.7	-109.2	-139.3	-56.7	-64.4	-67.9	-71.7	-105.5	-89.3
HEXAN		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	* $E_{solvatn}$	-29.7	-38.2	-48.6	-58.8	-78.5	-106.4	-45.4	-50.1	-53.5	-49.0	-94.9	-63.6

* *Same as the Van der Waals solvation energies* [$E_{solvatn}$(vdw)]

V.B STERIC ENERGIES WITH ELECTROSTATICS VERSUS THOSE WITHOUT ELECTROSTATICS

Contrary to the case when electrostatic and hydrogen bond energy is included in the calculations, table 4.15 show that solvated zinc complexes in the simulated organic phases are better solvated (and have better steric energies) than solvated zinc complexes simulated in the aqueous phase. This would predict better extraction of zinc complexes into benzene and hexane solvents, in agreement with experimental data.

Similar to the case when electrostatics is included in the calculations, the predicted better solvation of zinc complexes in benzene relative to those in hexane (table 4.15) parallels the experimental observation on CYANEX 921 whereby the solubility (a measure of the degree of solvation) of CYANEX 921 is higher in the aromatic diluents than in aliphatic diluents (1).

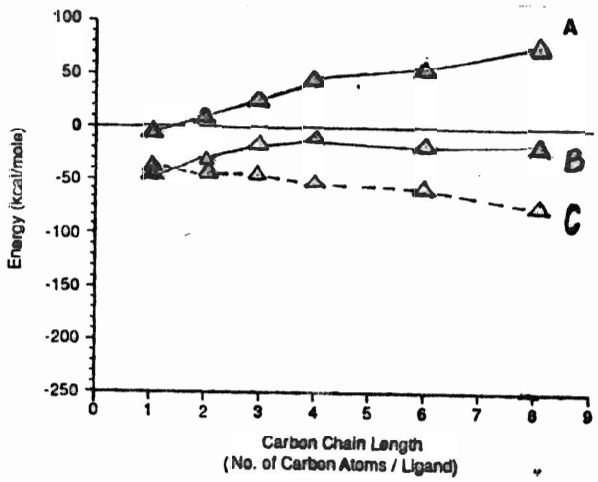
Steric and solvation energy data in tables 4.13 and 4.14 respectively was ploted against increasing carbon chain length for the ligands TMPO, TEPO, TNPPO, TBPO, THPO and TOPO as indicated in figure 4.3.

Figure 4.3: Plots Of Steric Energy Against Carbon Chain Length For Tetrahedral $ZnCl_2L_2$ Complexes In (I) Water (II) Benzene And (III) *n*-Hexane Minimized Without Electrostatics

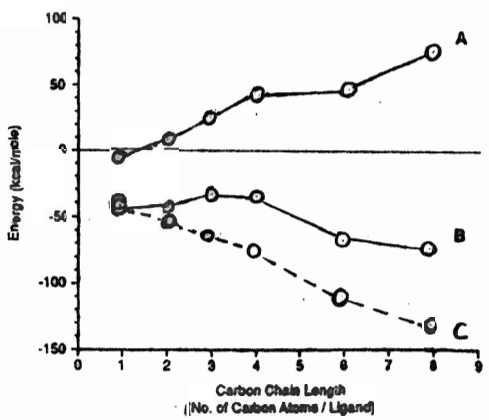
(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

A = Steric Energy Without Solvent Interactions; *B = Steric Energy With Solvent Interactions;*
C = Solvation Energy;

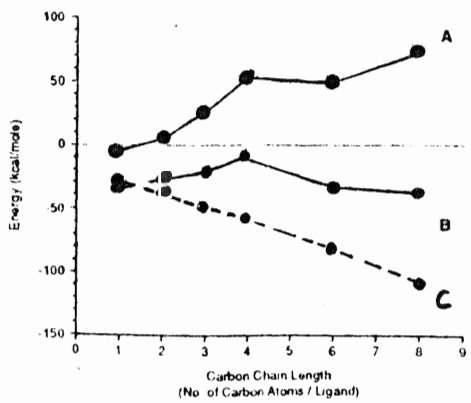
(I) WATER SYSTEM:



(II) BENZENE SYSTEM:



(III) HEXANE SYSTEM:



The trends observed here are similar to those in which electrostatic and hydrogen bond energy terms were included in the calculations; this is to say that in the simulated gas phase, the steric energy of the complex increases regularly with number of carbons in the alkyl group, whereas they go through a maximum when solvent-complex interactions are taken into account (figure 4.3). One exception here is that the steric energies for complexes in the organic phases is generally more favorable than those in the aqueous phase when electrostatics are excluded in the calculations (graph B of figure 4.3); also the energy gradient with increasing carbon chain length for the simulated solvation energy in the organic phases is steeper than the energy gradient in the simulated aqueous phase (graph C of figure 4.3). Therefore, when electrostatics are not included in the calculations, the prediction is that extraction into organic phase is favorable and becomes more so as the carbon chain length increases.

As opposed to the case when electrostatics are included in the calculations, calculations without electrostatics generally show that the complex steric energy of straight chain ligands is more favorable than that of complexes involving branched chain ligands (tables 4.13 and 4.14). However, judging from the calculations in which electrostatics were included, it is likely that branched chain systems will have better electrostatic energies and, hence, more favorable energies than is indicated by the calculations in which the electrostatic energy term is excluded.

V.C SIMULATED DISTRIBUTION COEFFICIENTS FROM STERIC ENERGIES WITHOUT ELECTROSTATICS

In the same sense that values for table 4.12 were determined, equation 4.4 was used in estimating the simulated distribution coefficients from steric energies without electrostatics. Such simulated distribution coefficients are given in table 4.16.

Table 4.16: Simulated Distribution Coefficient Values (D^*) For Tetrahedral $ZnCl_2L_2$ Complexes With No Electrostatics In The Energy Terms
(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

SYSTEM	CALC TYPE	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
		STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
BENZENE/ WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	D^*	**0.0**	**7.3**	**17.9**	**23.6**	**49.5**	**54.5**	**10.0**	**18.9**	**27.9**	**27.9**	**30.4**	**29.4**
HEXANE/ WATER		TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
	D^*	**0.0**	**0.0**	**3.7**	**0.0**	**17.3**	**20.8**	**0.0**	**5.0**	**13.1**	**2.1**	**10.4**	**0.8**

For the simulated distribution between benzene and water, table 4.16 show that extraction into benzene becomes more favorable as the carbon chain of the ligand increases from TMPO to TOPO; the simulated distribution between hexane and water show better extraction for complexes involving longer carbon chain (THPO and TOPO) than for those with shorter carbon chain length (TMPO to TBPO). This agrees with the experimental observation that the phosphine oxide ligands used in solvent extraction usually involve carbon chain length greater than three (1,3).

We also notice from table 4.16 that there is a significant variation in the simulated distribution coefficients among the complexes. This contradicts the experimental extraction data on related phosphonates and phosphinates (53) whereby it was found that varying the alkyl group has little effect on the extraction effectiveness of the extractant. However, it is likely that the experimental assertion (53) on phosphonates and phosphinates may not be extended to phosphine oxides because the three classes of phosphine extractants have been found to show significant differences in their extraction behavior (55).

Table 4.16 also show that extraction into benzene solvent is more favourable than in hexane solvent; once again, this is in line with the experimental observation on CYANEX 921 (1) whereby the solubility of CYANEX 921 is found to be higher in aromatic diluents than in aliphatic diluents.

The simulated distribution coefficients between benzene and water show good extraction for triphenylphosphine oxide (TPPO) complexes. This contradicts the experimental data on the extraction of zinc(II) by triphenylphosphine oxide (53) whereby the triphenylphosphine oxide show very poor extraction for zinc (II). This difference is mainly attributed to the fact that our calculations do not take into account the electronic inductive effects of the phenyl ligand; Preston and du Preez (53) attributes the poor extraction behavior of TPPO ligands to the electron withdrawing effects of the phenyl groups whereby the phenyl groups are presumed to withdraw electron density from the P-O group such that less electron density is available to the P-O group for effective coordination with the appropriate metal.

We can therefore generally say that correction factors for the electronic inductive effects need to be applied to the calculated distribution coefficient for a better fit of calculated to experimental data. Also, inclusion of accurate charges in the calculations or not including charges at all gives better simulation results.

VI CONCLUDING REMARKS

1) Increasing steric energy with increasing carbon chain length is counteracted by better solvation effects.
2) Extraction into organic solvents becomes better as the carbon chain length of the phosphine oxide ligand increases; however, due to excessive steric effects, extraction will become poor if the carbon chain length is incresed more than is necessary.
3) Extraction into benzene is more favorable than extraction into hexane.
4) Charges should only be included where these are accurately known; otherwise better simulation results are obtained without inclusion of charges; since charges for inorganic complexes are not well known and are rare in the literature, current molecular mechanics calculations on inorganic complexes will be better off without charges.
5) Accurate Ab initio or experimental charges and electronic inductive effects of the P-O group of the ligand is likely to reveal more information about the extraction effectiveness and selectivity of phosphine oxide ligands.

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APPENDICES

APPENDIX I: CALCULATED GEOMETRIES FOR TETRAHEDRAL $ZnCl_2L_2$ COMPLEXES

(L = Ligand as named below)

L	Name
TMPO	Trimethylphosphine oxide
TEPO	Triethylphosphine oxide
TNPPO	Tri-*n*-propylphosphine oxide
TBPO	Tri-*n*-butylphosphine oxide
THPO	Tri-*n*-hexylphosphine oxide
TOPO	Tri-*n*-octylphosphine oxide
TSPPO	Tri-*sec*-propylphosphine oxide
TTPO	Tri-*tert*-butylphosphine oxide
TIPO	Tri-*iso*-butylphosphine oxide
TSBPO	Tri-*sec*-butylphosphine oxide
TPOPO	Bis(2,4,4-trimethylpentyl)-*n*-octylphosphine oxide
TPPO	Triphenylphosphine oxide

Table I.1: Calculated Geometries For Tetrahedral $ZnCl_2(TMPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.498	1.491	1.496	1.497
P2-O2	1.499	1.495	1.498	1.497
M-O1	1.968	1.952	1.968	1.967
M-O2	1.969	1.955	1.968	1.969
P1-C1	1.812	1.798	1.809	1.807
P1-C2	1.813	1.810	1.809	1.811
P1-C3	1.813	1.817	1.810	1.812
P2-C4	1.812	1.806	1.809	1.808
P2-C5	1.812	1.809	1.810	1.809
P2-C6	1.815	1.812	1.813	1.813
ANGLES (degrees)				
M-O1-P1	141.5	136.1	140.1	140.2
M-O2-P2	143.8	136.1	140.4	140.3
O1-M-O2	113.0	112.0	113.6	112.3
Cl1-M-Cl2	110.9	123.7	112.2	110.7
Cl1-M-O1	106.0	96.2	104.8	104.2
Cl1-M-O2	108.2	115.0	110.7	108.4
Cl2-M-O1	107.8	103.0	107.3	107.1
Cl2-M-O2	110.8	106.5	108.2	113.7
O1-P1-C1	110.1	107.7	110.0	110.2
O1-P1-C2	110.2	111.6	110.4	110.6
O1-P1-C3	110.6	111.6	111.3	110.9
O2-P2-C4	109.8	107.9	108.9	109.4
O2-P2-C5	109.9	109.8	109.0	110.2
O2-P2-C6	111.0	110.7	112.1	112.1
C1-P1-C2	108.5	107.7	108.2	108.2
C1-P1-C3	108.7	109.0	108.3	108.3
C2-P1-C3	108.7	109.2	108.6	108.7
C4-P2-C5	108.6	107.8	108.7	106.9
C4-P2-C6	108.7	109.6	109.1	108.9
C5-P2-C6	108.9	111.1	109.1	109.2
TORSIONS (degrees)				
M-O1-P1-C1	65.1	84.3	60.4	63.1
M-O1-P1-C2	-54.5	-36.4	-59.4	-57.1
M-O1-P1-C3	-174.7	-156.2	-179.7	-177.1
M-O2-P2-C4	68.3	62.4	70.9	59.1
M-O2-P2-C5	-51.2	-57.0	-48.0	-58.1
M-O2-P2-C6	-171.3	-175.9	-168.4	180.0

Table I.2: Calculated Geometries For Tetrahedral $ZnCl_2(TEPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.498	1.501	1.497	1.498
P2-O2	1.499	1.502	1.499	1.502
M-O1	1.963	1.965	1.961	1.963
M-O2	1.964	1.973	1.964	1.967
P1-C1	1.824	1.827	1.823	1.822
P1-C2	1.826	1.829	1.824	1.824
P1-C3	1.827	1.833	1.824	1.824
P2-C4	1.824	1.825	1.822	1.822
P2-C5	1.826	1.827	1.822	1.824
P2-C6	1.828	1.831	1.824	1.825
ANGLES (degrees)				
M-O1-P1	141.1	138.0	139.5	142.7
M-O2-P2	144.2	144.4	143.5	144.5
O1-M-O2	105.2	99.9	106.2	106.7
Cl1-M-Cl2	113.2	118.1	114.9	108.8
Cl1-M-O1	106.6	103.6	104.9	108.9
Cl1-M-O2	111.9	116.6	111.8	110.3
Cl2-M-O1	107.6	106.1	109.5	110.9
Cl2-M-O2	111.8	111.1	109.6	111.2
O1-P1-C1	108.0	108.7	108.5	107.9
O1-P1-C2	109.4	108.7	109.5	110.8
O1-P1-C3	109.9	110.8	110.0	111.1
O2-P2-C4	106.0	105.5	106.7	106.1
O2-P2-C5	107.7	105.8	106.9	107.9
O2-P2-C6	108.2	108.3	109.3	108.3
C1-P1-C2	107.4	108.9	107.1	106.2
C1-P1-C3	110.7	109.8	109.7	109.7
C2-P1-C3	111.5	109.9	112.1	111.2
C4-P2-C5	110.1	111.6	110.0	111.3
C4-P2-C6	111.9	111.9	111.7	111.4
C5-P2-C6	112.5	113.2	112.0	111.6
TORSIONS (degrees)				
M-O1-P1-C1	72.7	72.7	73.8	65.4
M-O1-P1-C2	-49.2	-46.9	-48.8	-56.7
M-O1-P1-C3	-166.8	-166.4	-166.2	-174.5
M-O2-P2-C4	70.2	86.6	72.9	63.6
M-O2-P2-C5	-50.5	-33.6	-46.7	-56.1
M-O2-P2-C6	-171.7	-153.5	-168.1	-176.7

Table I.3: Calculated Geometries For Tetrahedral $ZnCl_2(TNPPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.507	1.505	1.499	1.505
P2-O2	1.508	1.511	1.506	1.505
M-O1	1.971	1.973	1.963	1.967
M-O2	1.972	1.978	1.971	1.970
P1-C1	1.831	1.834	1.830	1.832
P1-C2	1.833	1.834	1.831	1.832
P1-C3	1.833	1.835	1.832	1.832
P2-C4	1.829	1.821	1.827	1.828
P2-C5	1.832	1.830	1.829	1.829
P2-C6	1.834	1.837	1.831	1.834
ANGLES (degrees)				
M-O1-P1	147.2	147.0	146.6	147.4
M-O2-P2	147.8	150.7	148.6	148.6
O1-M-O2	113.0	114.9	112.0	112.0
Cl1-M-Cl2	109.5	102.5	111.8	111.0
Cl1-M-O1	103.3	99.2	104.1	102.8
Cl1-M-O2	108.5	110.6	113.3	108.2
Cl2-M-O1	110.2	113.8	104.5	111.0
Cl2-M-O2	111.9	114.0	110.7	111.5
O1-P1-C1	107.7	107.0	108.0	108.3
O1-P1-C2	108.7	108.7	108.6	108.3
O1-P1-C3	110.1	109.3	109.5	109.1
O2-P2-C4	106.7	104.7	106.5	106.1
O2-P2-C5	107.3	105.9	107.2	108.2
O2-P2-C6	107.9	110.2	108.4	108.4
C1-P1-C2	105.3	108.0	106.3	105.7
C1-P1-C3	112.3	110.9	112.1	112.4
C2-P1-C3	112.6	112.8	112.3	112.9
C4-P2-C5	110.0	110.2	110.6	109.8
C4-P2-C6	112.3	112.0	110.8	110.1
C5-P2-C6	112.4	113.4	113.0	113.9
TORSIONS (degrees)				
M-O1-P1-C1	32.2	36.1	32.6	35.2
M-O1-P1-C2	-91.0	-87.4	-89.7	-88.1
M-O1-P1-C3	154.1	156.3	154.6	157.4
M-O2-P2-C4	88.9	90.4	84.5	88.1
M-O2-P2-C5	-32.0	-28.8	-34.9	-31.4
M-O2-P2-C6	-152.6	-151.1	-156.9	-154.0

Table I.4: Calculated Geometries For Tetrahedral $ZnCl_2(TBPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.499	1.504	1.495	1.499
P2-O2	1.502	1.505	1.508	1.507
M-O1	1.964	1.965	1.957	1.963
M-O2	1.967	1.965	1.972	1.971
P1-C1	1.827	1.824	1.826	1.830
P1-C2	1.828	1.837	1.828	1.832
P1-C3	1.828	1.838	1.832	1.833
P2-C4	1.824	1.829	1.828	1.832
P2-C5	1.827	1.832	1.828	1.832
P2-C6	1.832	1.835	1.829	1.834
ANGLES (degrees)				
M-O1-P1	147.7	147.1	146.0	145.6
M-O2-P2	153.1	156.0	148.4	151.6
O1-M-O2	105.6	106.9	108.4	109.9
Cl1-M-Cl2	110.8	109.9	110.0	109.6
Cl1-M-O1	105.7	107.4	102.8	101.0
Cl1-M-O2	113.0	110.6	114.9	109.6
Cl2-M-O1	107.8	110.8	105.7	110.0
Cl2-M-O2	113.4	111.2	114.0	115.7
O1-P1-C1	107.4	103.9	108.5	108.2
O1-P1-C2	108.4	109.8	109.6	108.7
O1-P1-C3	109.4	112.7	110.6	111.7
O2-P2-C4	106.6	106.1	107.0	106.8
O2-P2-C5	107.3	108.1	107.7	107.5
O2-P2-C6	114.2	108.6	109.2	109.0
C1-P1-C2	107.4	107.0	105.5	103.0
C1-P1-C3	110.9	107.5	110.5	112.2
C2-P1-C3	113.2	115.8	112.1	113.0
C4-P2-C5	108.7	109.2	108.2	108.5
C4-P2-C6	109.0	110.7	109.0	109.8
C5-P2-C6	110.9	113.8	115.7	115.1
TORSIONS (degrees)				
M-O1-P1-C1	65.7	111.0	72.3	76.4
M-O1-P1-C2	-54.9	-15.1	-51.1	-48.9
M-O1-P1-C3	-171.7	-134.2	-167.0	-161.5
M-O2-P2-C4	65.2	70.4	71.6	76.6
M-O2-P2-C5	-58.2	-48.7	-46.2	-40.4
M-O2-P2-C6	-178.6	-165.7	-163.4	-159.4

Table I.5: Calculated Geometries For Tetrahedral $ZnCl_2(THPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.495	1.499	1.491	1.492
P2-O2	1.501	1.509	1.499	1.504
M-O1	1.960	1.963	1.959	1.959
M-O2	1.964	1.970	1.959	1.964
P1-C1	1.821	1.818	1.818	1.818
P1-C2	1.821	1.823	1.821	1.821
P1-C3	1.825	1.827	1.822	1.824
P2-C4	1.819	1.819	1.816	1.820
P2-C5	1.819	1.823	1.819	1.821
P2-C6	1.824	1.823	1.823	1.827
ANGLES (degrees)				
M-O1-P1	138.4	140.3	141.4	139.9
M-O2-P2	142.8	146.5	142.2	142.6
O1-M-O2	101.5	101.3	98.1	99.1
Cl1-M-Cl2	111.2	114.5	110.3	111.5
Cl1-M-O1	101.9	102.7	105.8	106.0
Cl1-M-O2	114.5	112.1	114.3	114.3
Cl2-M-O1	110.1	111.9	112.1	108.3
Cl2-M-O2	116.1	113.3	115.3	116.3
O1-P1-C1	108.1	108.4	106.1	107.9
O1-P1-C2	108.3	108.7	107.9	108.4
O1-P1-C3	108.5	109.8	109.5	109.0
O2-P2-C4	108.8	107.6	106.8	107.9
O2-P2-C5	108.8	110.8	109.9	110.3
O2-P2-C6	110.4	113.2	110.7	110.9
C1-P1-C2	109.5	108.7	109.4	108.3
C1-P1-C3	110.9	109.8	111.6	111.4
C2-P1-C3	111.5	111.4	112.1	111.7
C4-P2-C5	105.6	101.3	105.4	104.0
C4-P2-C6	111.3	111.2	111.5	111.3
C5-P2-C6	111.9	112.8	112.5	112.5
TORSIONS (degrees)				
M-O1-P1-C1	105.9	113.5	107.0	113.3
M-O1-P1-C2	-15.1	-6.6	-14.2	-7.8
M-O1-P1-C3	-135.3	-128.6	-134.0	-129.0
M-O2-P2-C4	67.0	52.5	63.6	60.5
M-O2-P2-C5	-48.4	-60.5	-52.5	-54.2
M-O2-P2-C6	-169.8	176.3	-173.6	-176.3

Table I.6: Calculated Geometries For Tetrahedral $ZnCl_2(TOPO)_2$

GOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.505	1.498	1.496	1.502
P2-O2	1.505	1.504	1.501	1.502
M-O1	1.967	1.965	1.960	1.963
M-O2	1.969	1.969	1.964	1.967
P1-C1	1.821	1.817	1.817	1.818
P1-C2	1.821	1.818	1.820	1.821
P1-C3	1.826	1.824	1.826	1.831
P2-C4	1.828	1.823	1.824	1.824
P2-C5	1.832	1.823	1.825	1.831
P2-C6	1.832	1.829	1.825	1.831
ANGLES (degrees)				
M-O1-P1	147.4	142.7	148.8	151.4
M-O2-P2	151.8	151.6	152.6	148.1
O1-M-O2	104.4	95.0	97.0	103.4
Cl1-M-Cl2	114.3	100.7	114.2	113.9
Cl1-M-O1	107.5	116.1	108.2	108.5
Cl1-M-O2	109.2	116.5	108.4	109.3
Cl2-M-O1	109.2	114.5	110.3	107.5
Cl2-M-O2	111.9	115.1	117.2	113.6
O1-P1-C1	106.9	108.1	106.4	106.7
O1-P1-C2	109.6	109.4	108.8	109.4
O1-P1-C3	111.8	110.8	111.5	111.6
O2-P2-C4	108.8	108.0	107.5	107.5
O2-P2-C5	108.9	110.5	109.4	109.1
O2-P2-C6	109.0	111.4	111.4	109.5
C1-P1-C2	106.7	107.1	107.1	106.5
C1-P1-C3	110.7	109.7	110.9	111.1
C2-P1-C3	110.9	111.8	112.0	111.4
C4-P2-C5	108.7	103.7	106.4	108.6
C4-P2-C6	109.7	111.3	110.5	110.9
C5-P2-C6	111.7	112.0	111.6	111.2
TORSIONS (degrees)				
M-O1-P1-C1	79.5	64.7	81.6	84.0
M-O1-P1-C2	-43.9	-56.3	-42.4	-39.4
M-O1-P1-C3	-164.0	-178.3	-161.9	-160.0
M-O2-P2-C4	80.3	92.0	93.4	79.7
M-O2-P2-C5	-41.7	-30.5	-30.4	-42.2
M-O2-P2-C6	-160.1	-145.3	-146.6	-159.9

Table I.7: Calculated Geometries For Tetrahedral $ZnCl_2(TSPPO)_2$

GOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.511	1.521	1.511	1.509
P2-O2	1.518	1.526	1.518	1.519
M-O1	1.972	1.971	1.969	1.969
M-O2	1.974	1.980	1.972	1.973
P1-C1	1.850	1.848	1.843	1.849
P1-C2	1.851	1.850	1.847	1.851
P1-C3	1.853	1.862	1.849	1.852
P2-C4	1.845	1.845	1.849	1.845
P2-C5	1.847	1.849	1.849	1.845
P2-C6	1.848	1.849	1.850	1.847
ANGLES (degrees)				
M-O1-P1	149.3	144.0	149.8	148.8
M-O2-P2	149.7	148.6	151.1	149.5
O1-M-O2	116.7	120.4	116.4	116.1
Cl1-M-Cl2	108.9	105.8	110.0	108.8
Cl1-M-O1	106.9	102.0	106.1	106.9
Cl1-M-O2	108.2	106.6	108.8	107.4
Cl2-M-O1	107.5	107.3	106.8	107.1
Cl2-M-O2	108.5	113.4	108.8	110.3
O1-P1-C1	105.8	107.3	103.1	106.2
O1-P1-C2	110.0	110.2	105.3	109.8
O1-P1-C3	110.7	110.6	106.4	110.8
O2-P2-C4	104.3	106.1	105.2	103.4
O2-P2-C5	105.0	106.4	110.3	105.0
O2-P2-C6	105.8	107.2	111.4	105.8
C1-P1-C2	106.3	106.9	113.3	106.1
C1-P1-C3	110.9	110.5	113.6	110.8
C2-P1-C3	112.9	111.4	114.0	113.0
C4-P2-C5	113.3	111.7	106.5	113.6
C4-P2-C6	113.4	112.3	110.0	113.7
C5-P2-C6	113.9	112.6	113.2	114.0
TORSIONS (degrees)				
M-O1-P1-C1	34.8	21.4	75.3	34.7
M-O1-P1-C2	-88.1	-102.2	-45.2	-88.0
M-O1-P1-C3	157.4	141.6	-165.4	157.7
M-O2-P2-C4	74.5	61.8	35.9	74.0
M-O2-P2-C5	-46.3	-58.4	-86.6	-46.9
M-O2-P2-C6	-165.6	-177.5	159.0	-166.3

Table I.8: Calculated Geometries For Tetrahedral $ZnCl_2(TTPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.516	1.521	1.514	1.516
P2-O2	1.526	1.522	1.528	1.527
M-O1	1.969	1.971	1.967	1.969
M-O2	1.974	1.974	1.974	1.974
P1-C1	1.892	1.887	1.891	1.834
P1-C2	1.893	1.888	1.893	1.889
P1-C3	1.893	1.894	1.894	1.893
P2-C4	1.888	1.892	1.886	1.884
P2-C5	1.889	1.895	1.887	1.887
P2-C6	1.889	1.897	1.888	1.889
ANGLES (degrees)				
M-O1-P1	152.3	151.8	151.6	151.6
M-O2-P2	160.3	160.0	158.8	159.4
O1-M-O2	119.1	118.0	121.1	118.9
Cl1-M-Cl2	109.6	108.2	109.4	108.7
Cl1-M-O1	99.9	100.8	99.5	98.6
Cl1-M-O2	108.5	104.3	107.8	109.7
Cl2-M-O1	107.1	107.2	107.3	107.3
Cl2-M-O2	112.3	117.1	111.2	113.1
O1-P1-C1	103.1	101.2	102.8	103.9
O1-P1-C2	105.3	106.0	105.7	105.4
O1-P1-C3	108.0	109.1	108.5	107.7
O2-P2-C4	101.9	101.5	102.1	102.3
O2-P2-C5	104.7	105.2	104.1	105.5
O2-P2-C6	107.1	105.8	107.5	106.9
C1-P1-C2	112.6	112.4	112.5	112.6
C1-P1-C3	113.1	112.6	112.8	113.0
C2-P1-C3	113.8	114.7	113.6	113.5
C4-P2-C5	113.6	113.0	113.1	113.1
C4-P2-C6	113.8	113.6	114.1	113.3
C5-P2-C6	114.2	116.0	114.6	114.5
TORSIONS (degrees)				
M-O1-P1-C1	93.7	93.4	93.3	87.8
M-O1-P1-C2	-27.4	-28.0	-27.6	-33.0
M-O1-P1-C3	-146.8	-146.6	-147.3	-152.6
M-O2-P2-C4	68.3	62.4	70.9	71.6
M-O2-P2-C5	-51.2	-57.0	-48.0	-50.6
M-O2-P2-C6	-171.3	-175.9	-168.4	-169.9

Table I.9: Calculated Geometries For Tetrahedral $ZnCl_2(TIPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.501	1.495	1.502	1.499
P2-O2	1.508	1.507	1.507	1.507
M-O1	1.962	1.957	1.961	1.962
M-O2	1.971	1.961	1.967	1.969
P1-C1	1.833	1.825	1.834	1.832
P1-C2	1.834	1.827	1.834	1.832
P1-C3	1.838	1.833	1.834	1.838
P2-C4	1.828	1.825	1.827	1.827
P2-C5	1.830	1.827	1.828	1.828
P2-C6	1.830	1.828	1.832	1.830
ANGLES (degrees)				
M-O1-P1	144.7	139.9	142.9	142.6
M-O2-P2	147.0	141.6	144.3	146.4
O1-M-O2	106.9	108.2	105.9	106.7
Cl1-M-Cl2	112.7	110.7	113.1	113.9
Cl1-M-O1	100.5	103.0	100.5	99.3
Cl1-M-O2	116.1	115.4	116.9	115.7
Cl2-M-O1	109.2	104.5	105.8	108.0
Cl2-M-O2	111.1	115.5	114.9	113.0
O1-P1-C1	107.1	107.2	106.7	106.5
O1-P1-C2	108.8	109.2	108.3	108.0
O1-P1-C3	111.5	110.0	108.4	109.2
O2-P2-C4	108.3	105.3	108.3	108.1
O2-P2-C5	109.1	108.7	109.7	108.6
O2-P2-C6	110.2	110.0	109.8	110.6
C1-P1-C2	105.4	103.5	105.4	104.4
C1-P1-C3	112.5	111.3	113.0	112.8
C2-P1-C3	114.9	115.6	114.9	115.8
C4-P2-C5	108.2	108.8	107.5	108.7
C4-P2-C6	108.8	110.0	108.2	109.3
C5-P2-C6	112.2	114.0	113.2	111.4
TORSIONS (degrees)				
M-O1-P1-C1	61.8	57.7	59.1	62.4
M-O1-P1-C2	-52.1	-55.2	-54.7	-50.6
M-O1-P1-C3	-174.0	-175.8	-176.7	-172.6
M-O2-P2-C4	101.4	107.5	106.3	104.6
M-O2-P2-C5	-16.1	-10.3	-10.8	-13.2
M-O2-P2-C6	-139.7	-133.5	-135.8	-135.8

Table I.10: Calculated Geometries For Tetrahedral $ZnCl_2(TSBPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.518	1.506	1.520	1.518
P2-O2	1.524	1.515	1.525	1.524
M-O1	1.975	1.963	1.975	1.973
M-O2	1.984	1.980	1.983	1.982
P1-C1	1.848	1.845	1.845	1.847
P1-C2	1.854	1.846	1.852	1.854
P1-C3	1.857	1.848	1.856	1.857
P2-C4	1.850	1.846	1.849	1.848
P2-C5	1.854	1.846	1.853	1.855
P2-C6	1.856	1.848	1.855	1.855
ANGLES (degrees)				
M-O1-P1	149.8	147.1	149.5	150.1
M-O2-P2	154.0	152.9	154.0	154.5
O1-M-O2	113.8	114.4	114.4	114.2
Cl1-M-Cl2	106.4	109.9	106.9	105.2
Cl1-M-O1	105.1	94.1	102.2	105.9
Cl1-M-O2	114.9	109.9	114.1	114.6
Cl2-M-O1	107.1	107.5	108.7	107.5
Cl2-M-O2	109.2	118.5	110.0	108.8
O1-P1-C1	105.8	105.4	106.7	105.5
O1-P1-C2	106.2	105.6	114.1	105.5
O1-P1-C3	113.4	113.9	104.6	114.2
O2-P2-C4	104.6	104.9	104.6	105.5
O2-P2-C5	107.2	106.4	107.1	107.5
O2-P2-C6	108.5	106.5	108.2	107.8
C1-P1-C2	108.4	106.6	108.1	108.6
C1-P1-C3	111.3	111.6	110.8	110.9
C2-P1-C3	111.7	113.8	112.4	112.2
C4-P2-C5	109.0	109.8	109.5	109.1
C4-P2-C6	111.2	113.5	111.8	111.5
C5-P2-C6	116.0	115.0	115.2	115.2
TORSIONS (degrees)				
M-O1-P1-C1	101.2	100.8	103.2	101.1
M-O1-P1-C2	-17.5	-15.8	-14.7	-18.0
M-O1-P1-C3	-140.0	-138.5	-137.5	-140.0
M-O2-P2-C4	76.1	73.9	74.8	74.7
M-O2-P2-C5	-47.6	-48.4	-48.0	-48.7
M-O2-P2-C6	-166.3	-169.0	-167.3	-167.9

Table I.11: Calculated Geometries For Tetrahedral $ZnCl_2(TPOPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.500	1.497	1.499	1.499
P2-O2	1.511	1.502	1.510	1.508
M-O1	1.965	1.959	1.965	1.965
M-O2	1.974	1.962	1.973	1.973
P1-C1	1.830	1.828	1.830	1.832
P1-C2	1.832	1.832	1.832	1.835
P1-C3	1.834	1.840	1.835	1.835
P2-C4	1.831	1.820	1.830	1.824
P2-C5	1.837	1.825	1.835	1.832
P2-C6	1.843	1.833	1.842	1.843
ANGLES (degrees)				
M-O1-P1	149.3	151.9	140.3	145.8
M-O2-P2	150.1	153.9	143.5	149.3
O1-M-O2	103.1	102.5	103.9	106.0
Cl1-M-Cl2	100.0	109.8	104.0	106.3
Cl1-M-O1	109.2	113.0	112.7	109.9
Cl1-M-O2	116.5	119.4	117.2	115.1
Cl2-M-O1	107.5	91.7	93.4	99.9
Cl2-M-O2	121.4	119.2	119.2	119.8
O1-P1-C1	108.0	106.6	108.3	108.0
O1-P1-C2	109.8	109.0	108.5	108.1
O1-P1-C3	110.9	109.4	110.1	112.4
O2-P2-C4	105.9	103.5	107.1	107.8
O2-P2-C5	109.6	109.5	109.2	108.6
O2-P2-C6	110.1	110.9	109.2	109.9
C1-P1-C2	105.4	107.1	105.6	105.7
C1-P1-C3	111.1	110.8	111.9	110.9
C2-P1-C3	111.4	113.7	112.4	111.4
C4-P2-C5	105.5	103.8	105.6	104.2
C4-P2-C6	112.3	113.0	112.3	112.3
C5-P2-C6	113.5	116.3	113.2	114.0
TORSIONS (degrees)				
M-O1-P1-C1	81.1	70.8	98.2	90.2
M-O1-P1-C2	-42.4	-54.1	-23.4	-32.6
M-O1-P1-C3	-164.4	-174.0	-146.8	-155.9
M-O2-P2-C4	69.1	51.6	60.2	63.2
M-O2-P2-C5	-46.5	-62.4	-53.8	-50.3
M-O2-P2-C6	-167.8	173.1	-176.9	-172.9

Table I.12: Calculated Geometries For Tetrahedral $ZnCl_2(TPPO)_2$

GEOMETRY TYPE	CALCULATED GEOMETRIES			
	unsolvated complex	in water	in benzene	in *n*-hexane
BONDS (Å)				
P1-O1	1.504	1.499	1.500	1.502
P2-O2	1.505	1.507	1.503	1.510
M-O1	1.963	1.960	1.959	1.960
M-O2	1.964	1.964	1.963	1.969
P1-C1	1.828	1.824	1.828	1.828
P1-C2	1.830	1.825	1.829	1.829
P1-C3	1.833	1.825	1.833	1.836
P2-C4	1.828	1.830	1.824	1.829
P2-C5	1.833	1.831	1.829	1.830
P2-C6	1.833	1.831	1.830	1.831
ANGLES (degrees)				
M-O1-P1	157.2	153.4	156.4	157.9
M-O2-P2	160.0	159.8	158.6	161.6
O1-M-O2	88.1	90.5	88.4	89.6
Cl1-M-Cl2	113.9	128.3	114.7	114.0
Cl1-M-O1	110.9	101.5	110.9	108.4
Cl1-M-O2	112.3	117.0	112.0	112.3
Cl2-M-O1	114.2	103.4	112.6	110.9
Cl2-M-O2	114.9	109.5	115.4	118.7
O1-P1-C1	106.7	107.3	107.2	107.1
O1-P1-C2	109.6	108.9	109.0	111.0
O1-P1-C3	110.5	112.6	110.2	111.1
O2-P2-C4	105.9	103.6	105.8	104.4
O2-P2-C5	109.2	110.6	109.7	109.8
O2-P2-C6	110.7	113.1	110.7	111.2
C1-P1-C2	109.0	106.9	109.8	106.9
C1-P1-C3	110.4	108.7	110.0	107.4
C2-P1-C3	110.6	112.5	110.7	113.4
C4-P2-C5	110.2	109.0	109.9	109.6
C4-P2-C6	110.4	109.5	110.2	110.4
C5-P2-C6	110.4	110.9	110.6	111.3
TORSIONS (degrees)				
M-O1-P1-C1	66.6	64.1	66.9	67.4
M-O1-P1-C2	-55.2	-54.3	-54.7	-52.0
M-O1-P1-C3	-175.5	-173.9	-174.4	-176.4
M-O2-P2-C4	75.2	66.9	79.4	80.6
M-O2-P2-C5	-46.5	-56.3	-42.1	-43.1
M-O2-P2-C6	-165.9	-174.2	-161.8	-161.1

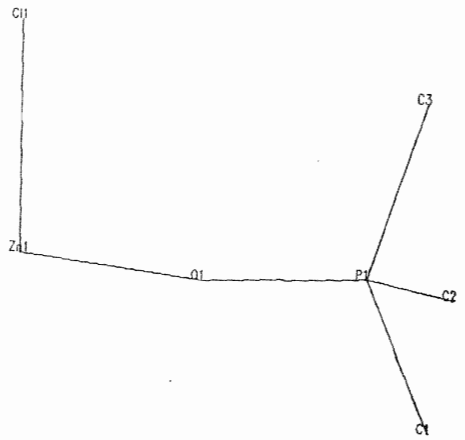
APPENDIX II: CALCULATED CHARGES FOR TETRAHEDRAL $ZnCl_2L_2$ COMPLEXES

(L = Ligand as named on page 110)

Figure II.1: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TMPO)_2$

(Only the unique part of the molecule [ZnClTMPO] is shown)

SUBSTRUCTURE



ASSOCIATED CHARGES

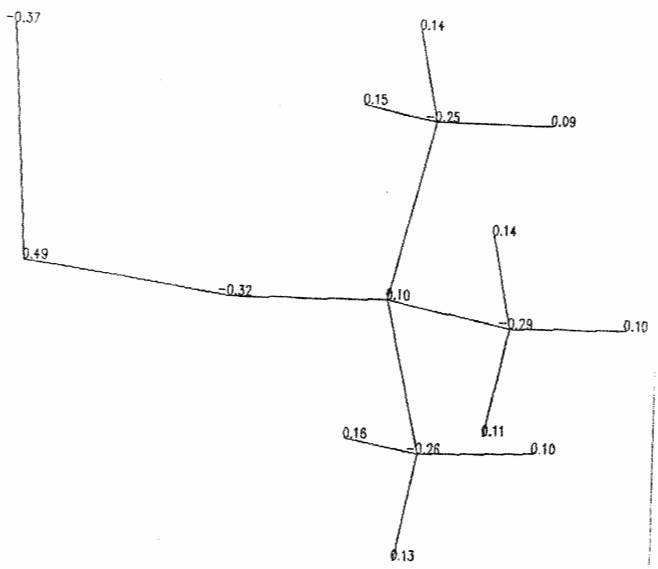
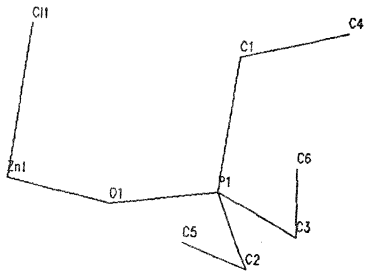


Figure II.2: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TEPO)_2$

(Only the unique part of the molecule [ZnClTEPO] is shown)

SUBSTRUCTURE



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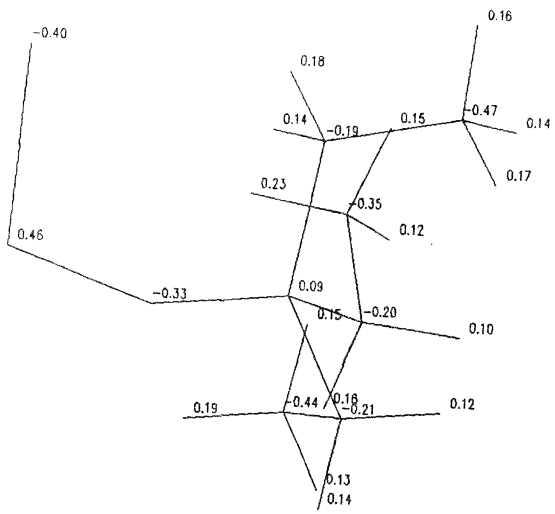
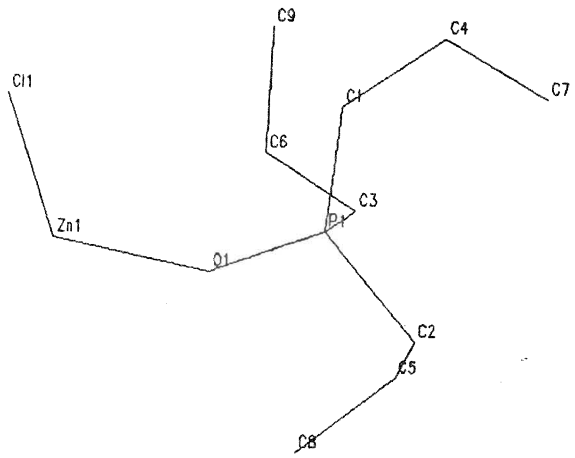


Figure II.3: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TNPPO)_2$

(Only the unique part of the molecule [ZnClTNPPO] is shown)

SUBSTRUCTURE



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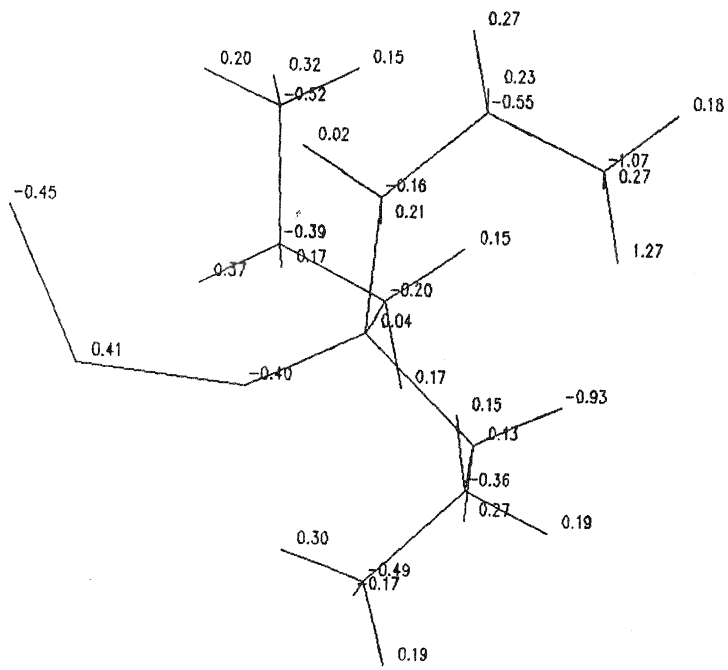
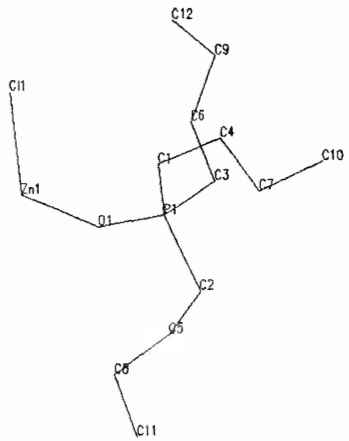


Figure II.4: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TBPO)_2$

(Only the unique part of the molecule [ZnClTBPO] is shown)

SUBSTRUCTURE



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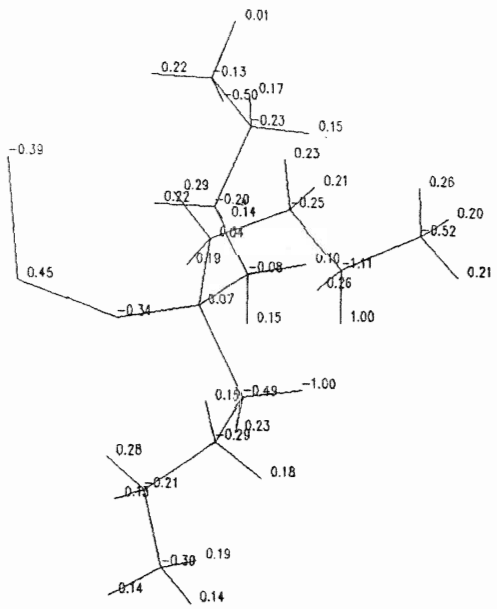
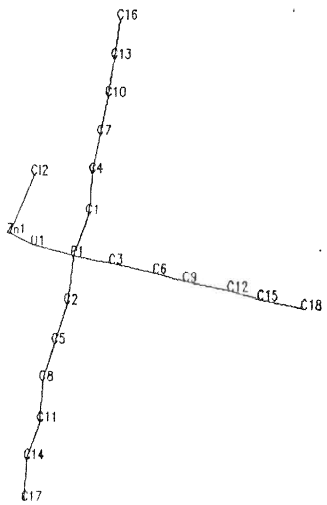


Figure II.5: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(THPO)_2$

(Only the unique part of the molecule [ZnClTHPO] is shown)

SUBSTRUCTURE



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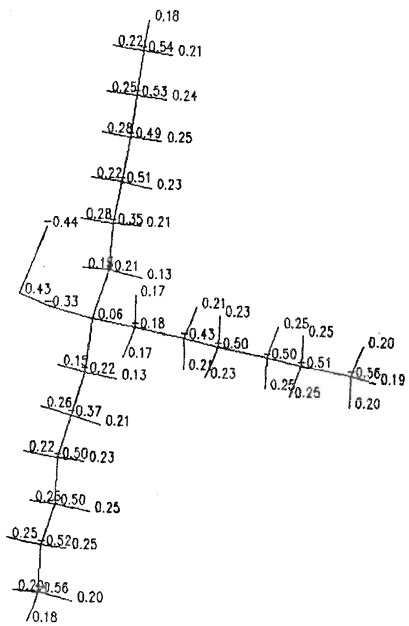
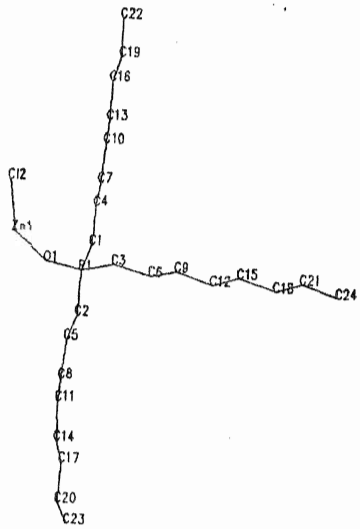


Figure II.6: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TOPO)_2$

(Only the unique part of the molecule [ZnClTOPO] is shown)

SUBSTRUCTURE



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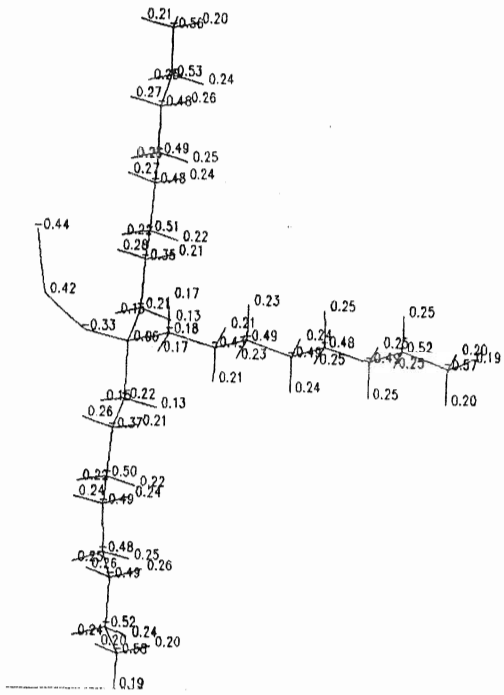
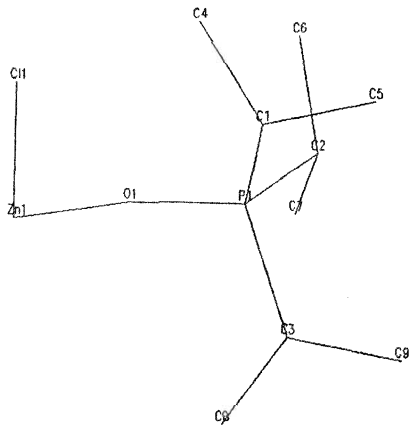


Figure II.7: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TSPPO)_2$

(Only the unique part of the molecule [ZnClTSPPO] is shown)

SUBSTRUCTURE



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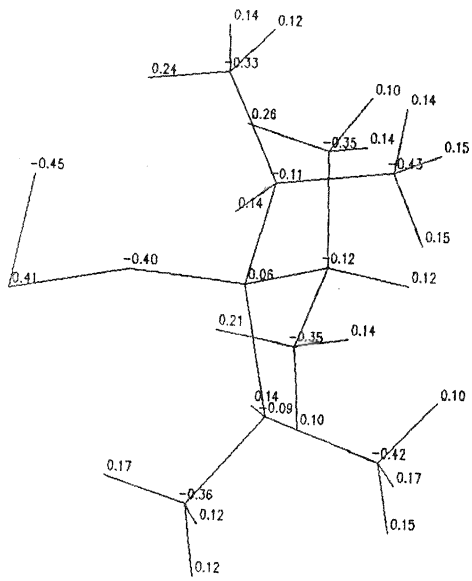
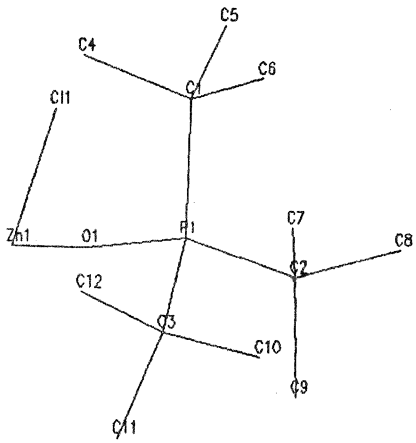


Figure II.8: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TTPO)_2$

(Only the unique part of the molecule [ZnClTTPO] is shown)

SUBSTRUCTURE



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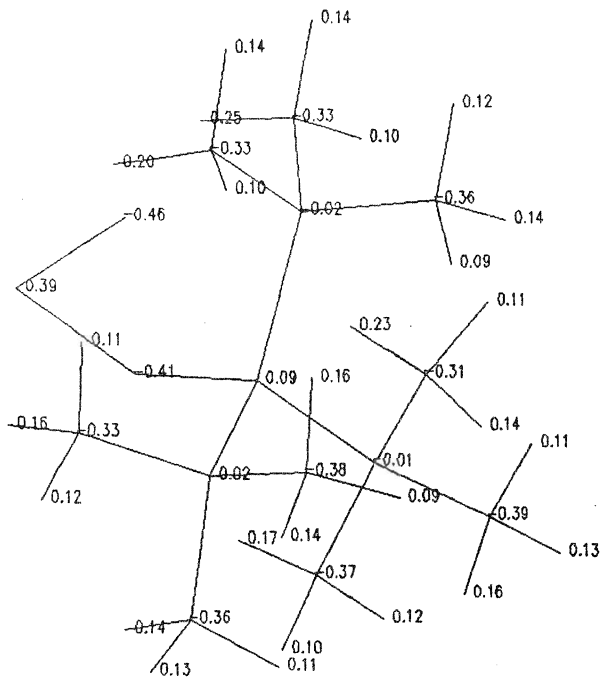
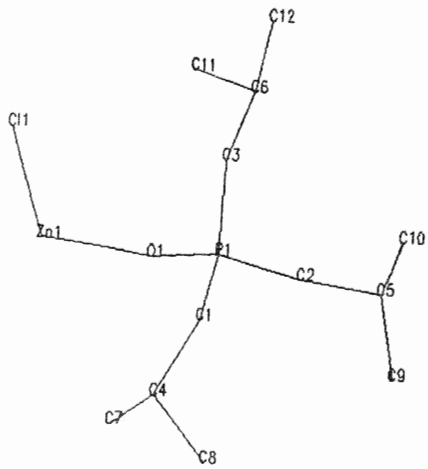


Figure II.9: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TIPO)_2$

(Only the unique part of the molecule [ZnClTIPO] is shown)

SUBSTRUCTURE



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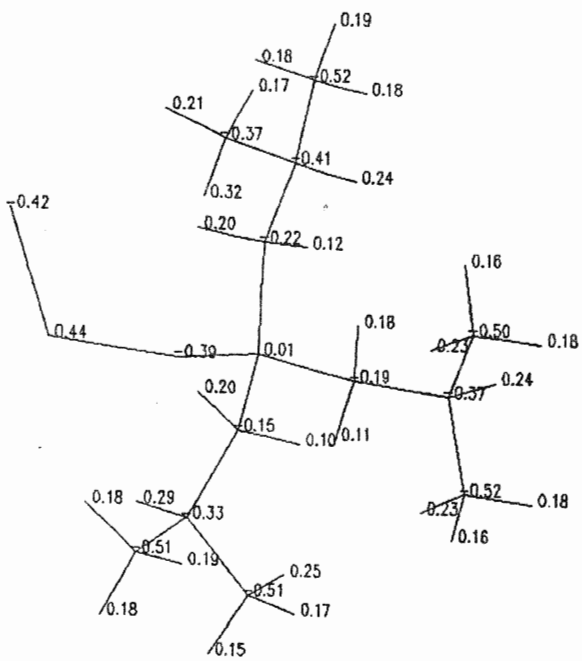
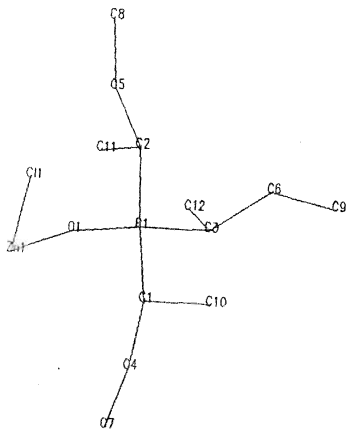


Figure II.10: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TSBPO)_2$

(Only the unique part of the molecule [ZnClTSBPO] is shown)

SUBSTRUCTURE



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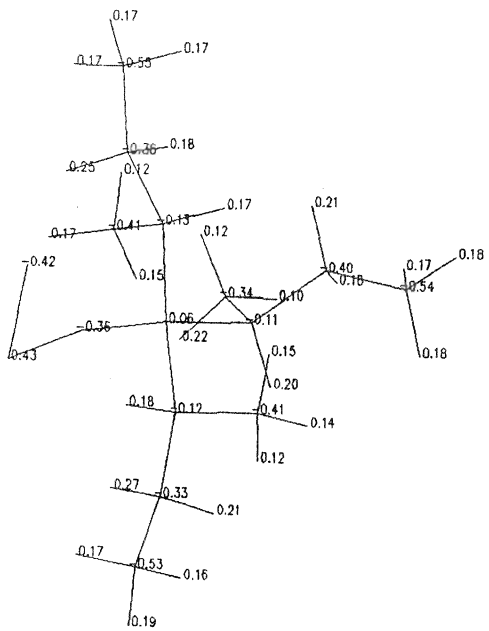
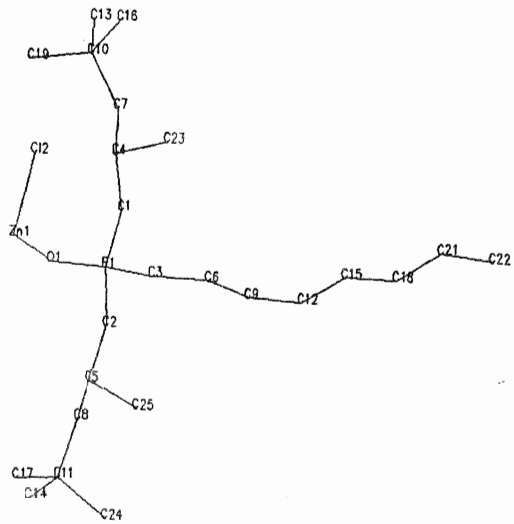


Figure II.11: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TPOPO)_2$

(Only the unique part of the molecule [ZnClTPOPO] is shown)

SUBSTRUCTURE



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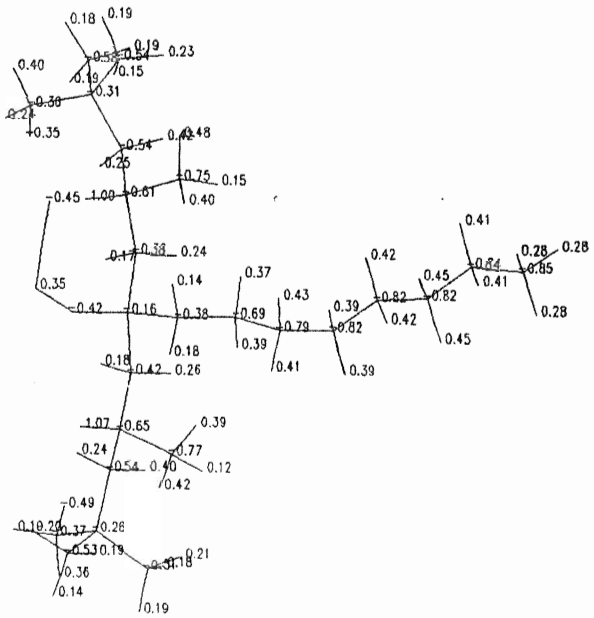
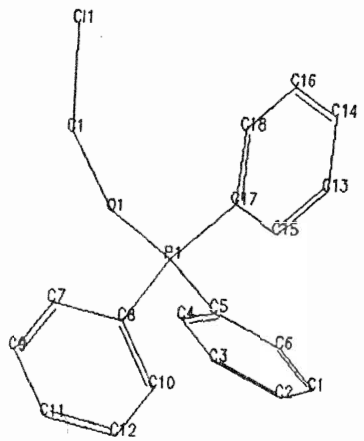


Figure II.12: Calculated Charges For Unsolvated Tetrahedral $ZnCl_2(TPPO)_2$

(Only the unique part of the molecule [ZnClTPPO] is shown)

SUBSTRUCTURE



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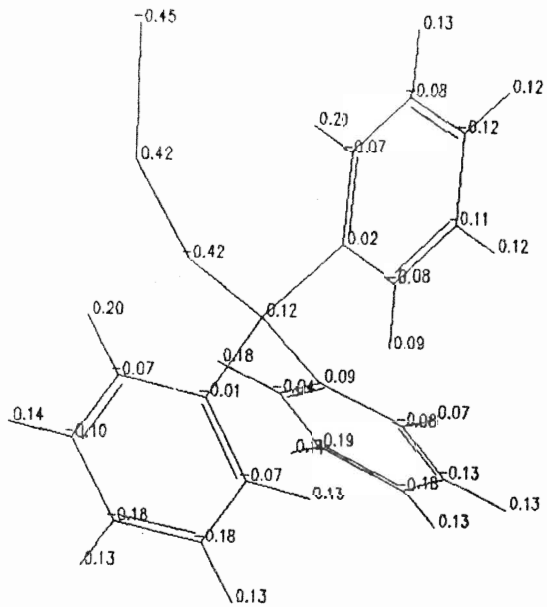

APPENDIX III: CAMBRIDGE STRUCTURE DATABASE (CSD) INFORMATION ON PHOSPHINE OXIDES

Abbreviations Used In Tables III.3 To III.8 Are As Follows:

RF = Crystallographic refinement factor

AS = Average sigma for C-C bonds:

0 = unspecified

1 = 0.001 to 0.005

2 = 0.006 to 0.010

3 = 0.011 to 0.030

4 = 0.031 and above

ERR = Error status of the publication:

0 = no errors detected

1 = entry contains one or more errors

CN = Coordination Number

Table III.1: CSD Bibliographic Information On Triphenylphosphine Oxide Complexes

No.	Ref. Code	Compoud Name Source Reference
1	ACPOSN	ACETATO-TRICHLORO-(TRIPHENYLPHOSPHINE OXIDE) TIN(IV) M. MASAKI, S. MATSUNAMI, K.OKIMOTO, H. UEDA, *Chem. Lett.*, 1978, 119
2	AIXPOU	ACETONE-BIS(ISOTHIOCYANATO)-DIOXO-BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM(VI) G. BOMBIERI, E. FORSELLINI, G. DE PAOLI, D. BROWN, T.C. TSO, *J. Chem. Soc., Dalton,* 1979, 2042
3	BEBHIZ	DINITRATO-DIOXO-BIS(TRIPHENYLPHOSPHINE OXIDE) NEPTUNIUM(VI) N.W. ALCOCK, M.M. ROBERTS, D. BROWN, *J. Chem. Soc., Dalton,* 1982, 25
4	BEBHUL	DICHLORO-DIOXO-(TRIPHENYLPHOSPHINE OXIDE) NEPTUNIUM(VI) N.W. ALCOCK, M.M. ROBERTS, D. BROWN, *J. Chem. Soc., Dalton,* 1982, 25
5	BIJWEW	DICHLORO-BIS(TRIPHENYLPHOSPHINE-OXIDE) ZINC(II) C.A.KOSKY,J.-P.GAYDA,J.F.GIBSON,S.F.JONES,D.J.WILLIAMS, *Inorg.Chem.*, 1982(21), 3173
6	BIJWIA	DIBROMO-BIS(TRIPHENYLPHOSPHINE OXIDE) ZINC(II) M. MASAKI, S. MATSUNAMI, K.OKIMOTO, H. UEDA, *Chem. Lett.*, 1978, 119
7	BIRXIJ	BIS(TRIPHENYLPHOSPHINE OXIDE)-DINITRATO COBALT(II) A.M.G.D. RODRIGUES, R.H.P. FRANCISCO, J.R. LECHAT, *Cryst. Struct. Commun.*, 1982(11), 847
8	BOFHIN	(μ-4-OXO)-HEXAKIS(μ-2-CHLORO)-TETRAKIS((TRIPHENYLPHOSPHINE OXIDE)--COPPER(II)) DICHLOROMETHANE SOLVATE YU. A. SIMONOV, A.A. DVORKIN, M.A. YAMPOL'SKAYA, V.E. ZAVODNIK, *Zh. Neorg. Khim.*, 1982(27), 1220
9	BOMGAL	TRANS- TETRABROMO-BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM(IV) G. BOMBIERI, F. BENETOLLO, K.W. BAGNALL, M.J. PLEWS, D. BROWN, *J. Chem. Soc.,Dalton,* 1983, 343

No.	Ref. Code	Compoud Name Source Reference
10	BOZWES	AQUA-BIS(1,2-NAPHTHOQUINONE-1-OXIMATO-O,N)-(TRIPHENYLPHOSPHINE--OXIDE)-DIOXO URANIUM(VI) R. GRAZIANI, U. CASELLATO, P.A. VIGATO, S. TAMBURINI, M. VIDALI, *J. Chem. Soc. D.* 1983, 697
11	CACPOU	BIS(3-CHLOROPENTANE-2,4-DIONATO)-DIOXO-(TRIPHENYLPHOSPHINE OXIDE) URANIUM(VI) J.C. TAYLO, A.B. MCLAREN, *J. Chem. Soc., Dalton,* 1979, 460
12	CADMAV	TRICHLORO-NITROSYL-(TRIPHENYLPHOSPHINIMINATO)-(TRIPHENYLPHOSPHINE OXY) RHENIUM DICHLOROMETHANE SOLVATE N. MRONGA, F. WELLER, K. DEHNICKE, *Z. Anorg. Allg. Chem.*, 1983(502), 35
13	CDXUPO	DICHLORODIOXO -BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM(VI) G. BOMBIERI, E. FORSELLINI, J.P. DAY, W.I. AZEEZ, *J. Chem. Soc.,Dalton*, 1978, 677
14	CECNUT	DIPOTASSIUM (μ-2-OXO)-BIS((1,2-BIS(3,5-DICHLORO-2-HYDROXYBENZAMIDO)--ETHANE-N,N',O,O')-(TRIPHENYLPHOSPHINE OXIDE-O) OSMIUM) ACETONE SOLVATE MONOHYDRATE J.A. CHRISTIE, T.J. COLLINS, T.E. KRAFFT, B.D. SANTARSIERO, G.H. SPIES, *J. Chem. Soc., Chem. Comm.*, 1984, 198
15	CECYAK	BROMO-(TRIPHENYLPHOSPHINE OXIDE)-TRIS(3-THIENYL) TIN D.W. ALLEN, D.J. DERBYSHIRE, I.W. NOWELL, J.S. BROOKS, *J. Organomet. Chem.*, 1984(260), 263
16	CEKTAN	TRIBROMO-BIS(TRIPHENYLPHOSPHINE OXIDE) THALLIUM(III) S.E. JEFFS, R.W.H. SMALL, I.J. WORRAL, *Acta Cryst., C (Cr. Str. Comm.),* 1984(40), 381
17	CEKTAN01	TRIBROMO-BIS(TRIPHENYLPHOSPHINE OXIDE) THALLIUM(III) M.R. BERMEJO, F. BOTANA, M. GAYOSO, A. CASTIREIRAS, W. HILLER, J. STRAHLE, *Acta Cientifica Compostelana,* 1985(22), 161

No.	Ref. Code	Compoud Name Source Reference
18	CFPOTL	DI-μ-CHLORO-BIS(BIS(2,3,5,6-TETRAFLUOROPHENYL)-(TRIPHENYLPHOSPHINE OXIDE) THALLIUM(III)) K. HENRICK, M. MCPARTLIN, R.W. MATHEWS, G.B. DEACON, R.J. PHILLIPS, *J. Organomet. Chem.*, 1980(193), 13
19	CIWHIZ10	ETHYL-TRICHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) TIN(IV) A.I. TURSINA, L.A. ASLANOV, S.V. MEDVEDEV, A.V. YATSENKO, *Koord. Khim.*, 1985(11), 417
20	CLOPHW	TRICHLORO-OXO-BIS(TRIPHENYLPHOSPHINE OXIDE) TUNGSTEN(V) L.H. HILL, N.C. HOWLADER, F.E. MABBS, M.B. HURSTHOUSE, K.M.A. MALIK, *J. Chem. Soc.,Dalton*, 1980, 1475
21	CLPHOV	DICHLORO-OXO-BIS(TRIPHENYLPHOSPHINE OXIDE-O) VANADIUM(IV) M.R. CAIRA, B.J. GELLATLY, *Acta Crystallogr.,Sect. B*, 1980(36), 1198
22	CLPOMN10	CHLORO-ISOTHIOCYANATO-BIS(TRIPHENYLPHOSPHINE OXIDE) MANGANESE(II) K. TOMITA, *Acta Cryst., C (Cr. Str. Comm.)*, 1987(43), 1628
23	CLPOZN	DICHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) ZINC(II) J.P. ROSE, R.A. LALANCETTE, J.A. POTENZA, H.J. SCHUGAR, *Acta Crystallogr.,Sect. B*, 1980(36), 2409
24	CLTPOC10	BIS(TRIPHENYLPHOSPHINE OXIDE)-DICHLORO COBALT(II) Y.P. MASCARENHAS, *To Be Published*, 1980
25	COJYEF	OXO-TRICHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) NIOBIUM(V) V.S. SERGIENKO, M.A. PORAI-KOSHITS, A.A. KONOVALOVA, V.V. KOVALEV, *Koord. Khim..*, 1984(10), 1116
26	CONTEE	TRANS-BIS(SULFUR DIOXIDE)-TETRAKIS(TRIPHENYLPHOSPHINE OXIDE) MANGANESE(II) DI-IODIDE G.A. GOTT, J. FAWCETT, C.A. MCAULIFFE, D.R. RUSSELL, *J. Chem. Soc., Chem. Comm.*, 1984, 1283

No.	Ref. Code	Compoud Name Source Reference
27	CPPOCU01	(μ-4-OXO)-HEXAKIS(μ-2-CHLORO)-TETRAKIS(TRIPHENYLPHOSPHINE OXIDE)--TETRA-COPPER(II) A.A. DVORKIN, YU. A. SIMONOV, M.A. YAMPOL'SKAYA, T.I. MALINOVSKII, *Kristallografiya*, 1983(28), 811
28	CPPOCU02	(μ-4-OXO)-HEXAKIS(μ-2-CHLORO)-TETRAKIS(TRIPHENYLPHOSPHINE OXIDE)--TETRA-COPPER(II) NITROMETHANE SOLVATE I.P. KONDRATYUK, YU. A. SIMONOV, M.A. YAMPOL'SKAYA, L.A. MURADYAN, V.I. SIMONOV, *Kristallografiya*, 1986(31), 682
29	CTPOCU	DICHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) COPPER(II) J.A. BERTRAND, A.R. KALYANARAMAN, *Inorg. Chim. Acta,* 1971(5), 341
30	CTPOXB10	TRICHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) ANTIMONY(III) L. GOLIC, S. MILICEV, *Acta Crystallogr.,Sect. B,* 1978(34), 3379
31	CUPSEL	CIS-(μ-2-ETHYLENEDIOLATO)-BIS(BIS(ETA-5-PENTAMETHYL CYCLOPENTADIENYL)-TRIPHENYLPHOSPHINE OXIDE SAMARIUM) TOLUENE SOLVATE W.J. EVANS, J.W. GRATE, R.J. DOEDENS, *J. Am. Chem. Soc.,* 1985(107), 1671
32	CUPSIP	TRANS-(μ-2-ETHYLENEDIOLATO)-BIS(BIS(ETA-5-PENTAMETHYL CYCLOPENTADIENYL)-TRIPHENYLPHOSPHINE OXIDE SAMARIUM) W.J. EVANS, J.W. GRATE, R.J. DOEDENS, *J. Am. Chem. Soc.,* 1985(107), 1671
33	CXPHOW	DICHLORODIOXO-BIS(TRIPHENYLPHOSPHINE OXIDE) TUNGSTEN(VI) J.F. DE WET, M.R. CAIRA, B.J. GELLATLY, *Acta Crystallogr.,Sect. B,* 1978(34), 762
34	DALYAQ	DIOXO-BIS(PENTAFLUOROBENZOATO)-BIS(TRIPHENYLPHOSPHINE OXIDE URANIUM(VI) T-BUTANOL SOLVATE G.B. DEACON, P.I. MACKINNON, J.C. TAYLOR, *Polyhedron*, 1985(4), 103
35	DAPNEN	TETRACHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) TIN A.I. TURSINA, L.A. ASLANOV, S.V. MEDVEDEV, A.V. YATSENKO, *Koord. Khim.,* 1985(11), 417
36	DBTPOC	DIBROMO-BIS(TRIPHENYLPHOSPHINE OXIDE) COPPER(II) J.A. BERTRAND, S.L. GRAHAM, H.M. DEUTSCH, D.G. VANDERVEER, *Inorg. Chim. Acta,* 1976(19), 189 D. PERIOTTO, S.A. ANTONIO, K. TOMITA, *Ecletica Quim.,* 1983(11), 8

No.	Ref. Code	Compoud Name Source Reference
37	DEGGIF10	DICHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) MANGANESE(II) K. TOMITA, *Acta Cryst.,C (Cr. Str. Comm.),* 1985(41), 1832
38	DESREY	TETRAKIS(TETRAHYDROBORATO)-BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM(IV) BENZENE SOLVATE P. CHARPIN, M. LANCE, E. SOULIE, D. VIGNER, H. MARQUET-ELLIS, *Acta Cryst.,C (Cr. Str. Comm.),* 1985(41), 1723
39	DEVYIM	BIS(μ-2-IODO)-BIS(IODO-(TRIPHENYLPHOSPHINE OXIDE) COBALT(II) BENZENE SOLVATE S. GORTA, W. HINRICHS, J. REEDIJK, J. RIMBAULT, J.C. PIERRARD, R.P. HUGEL, *Inorg. Chim. Acta,* 1985(105), 181
40	DILWUQ	TETRAKIS (μ-2--3-CHLOROPROPANOATO-O,O')-BIS(TRIPENYLPHOSPHINE OXIDE) DI-COPPER(II) P. SHARROCK, M. MELNIK, F. BELANGER-GARIEPY, A.L. BEAUCHAMP, *Can J. Chem.,* 1985(63), 2564
41	DIRSOM	DICHLORO-DIETHYL-BIS(TRIPENYLPHOSPHINE OXIDE) TIN A.I. TURSINA, L.A. ASLANOV, V.V. CHERNYSHEV, S.V. MEDVEDEV, A.V. YATSENKO, *Koord. Khim.,* 1985(11), 1420
42	DOBMAI	CIS-BIS(μ-2--ACETATO-O,O')-(μ-2--1-PYRROLECARBODITHIOLATO-S,S')) - TRIPHENYLPHOSPHINE OXIDE-O) DI-MOLYBDENUM BENZENE SOLVATE D.M. BAIRD, P.E. FANWICK, T. BARWICK, *Inorg. Chem.,* 1985(24), 3753
43	DOLSUS	CHLORO-DIOXO-(TRICHLORO-ACETATO-O,O')-BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM DICHLOROMETHANE SOLVATE N.W. ALCOCK, D.J. FLANDERS, K.W. BAGNALL, I. AHMED, *Acta Cryst., C(Cr. Str. Comm.),* 1986(42), 634
44	DOTDEV	TETRAKIS(TRIPHENYLPHOSPHINE OXIDE)-TRI-ISOTHIOCYANATO NEODYMIUM HUANG CHUNHUI, XU RONGFANG, XU XIAOJIE, XU GUANGXIAN, *J. Inorg. Chem. (Chinese),* 1985(1), 103
45	DOWLIK	TRIS(ETA-5--METHYLCYCLOPENTADIENYL)-(TRIPHENYLPHOSPHINE OXIDE) URANIUM(III) J.G. BRENNAN, R.A. ANDERSEN, A. ZALKIN, *Inorg. Chem.,* 1986(25), 1761

No.	Ref. Code	Compoud Name Source Reference
46	DUHTIJ	CIS-TETRA-IODO-BIS(TRIPHENYLPHOSPHINE OXIDE) TIN A.I. TURSINA, L.A. ASLANOV, V.V. CHERNYSHEV, S.V. MEDVEDEV, A.V. YATSENKO, *Koord. Khim.*, 1986(12), 420
47	DUHTOP	ETHYL-TRI-IODO-BIS(TRIPHENYLPHOSPHINE OXIDE) TIN A.I. TURSINA, L.A. ASLANOV, V.V. CHERNYSHEV, S.V. MEDVEDEV, A.V. YATSENKO, *Koord. Khim.*, 1986(12), 420
48	DUHVAD	HEXAKIS(μ-2--TRIFLUOROACETATO-O,O')-(μ-3--OXO)-TRIS(TRIPHENYLPHOSPHIN OXIDE)-IRON(II)-DI-IRON(III) A.I. TURSINA, L.A. ASLANOV, V.V. CHERNYSHEV, S.V. MEDVEDEV, A.V. YATSENKO, *Koord. Khim.*, 1986(12), 398
49	DORDOJ	(DINITRATO-O,O')-BIS(TRIPHENYLPHOSPHINE OXIDE) COPPER(II) TOLUENE SOLVATE M.B. FERRARI, G.F. GASPARRI, G. PELIZZI, P. TARASCONI, *Acta Cryst., C(Cr. Str. Comm.)*, 1986(42), 634
50	DUVSOC	BIS(NITRATO-O)-TRIPHENYLPHOSPHINE--TRIPENYLPHOSPHINE OXIDE) PALLADIUM(II) C.J. JONES, J.A. MCCLEVERTY, A.S. ROTHIN, H. ADAMS, N.A. BAILEY, *J. Chem. Soc., Dalton*, 1986, 2055
51	DUZDOR	DIBROMO-IODO-BIS(TRIPHENYLPHOSPHINE OXIDE-O) THALLIUM(III) A. CASTINEIRAS, W. HILLER, M.R. BERMEJO, M. GAYOSO, *Acta Cryst., C(Cr. Str. Comm.)*, 1986(42), 1289
52	FABMUQ10	ANTI-BIS(DICHLORO-(μ-2--(2-METHYL-1-PROPANETHIOLATO-S))-OXO-(TRIPHENYLPHOSPHINE OXIDE-O) TUNGSTEN(V)) DICHLOROMETHANE SOLVATE J.M. BALL, P.M. BOORMAN, J. F. RICHARDSON, *Inorg. Chem.*, 1986(25), 3325
53	FAKDUQ	POTASSIUM BIS(TETRABROMOCATECHOLATO)-(TRIPHENYLPHOSPHINE OXIDE) MANGANESE(III) DIHYDRATE ACETONE SOLVATE S.K. LARSEN, C.G. PIERPONT, G. DEMUNNO, G. DOLCETTI, *Inorg. Chem.*, 1986(25), 4828

No.	Ref. Code	Compoud Name Source Reference
54	FELHAF	TETRABROMO-BIS(TRIPHENYLPHOSPHINE OXIDE-O) TIN A.I. TURSINA, A.V. YATSENKO, S.V. MEDVEDEV, V.V. CHERNYSHEV, L.A. ASLANOV, *Zh. Strukt. Khim.*, 1986(27), 157-5
55	FICPUC	(DIBENZOYLMETHANATO-O,O')-TRIS(NITRATO-O,O')-BIS(TRIPHENYLPHOSPHINE OXIDE-O) THORIUM(IV) LUO BAOSHENG, CHEN LIAORONG, ZHU WENXIANG, YIN SHOUYI, *J. Struct. Chem.*, 1987(6), 173
56	FILCEI	TRIBROMO-ETHYL-BIS(TRIPHENYLPHOSPHINE OXIDE) TIN A.I. TURSINA, S.V. MEDVEDEV, A.V. YATSENKO, L.A. ASLANOV, *Zh. Strukt. Khim.*, 1987(28), 90-1
57	FILHAF	TRIS(TETRAHYDROBORATO-H,H',H'')--(TETRAHYDROBORATO-H,H') BIS(TRIPHENYLPHOSPHINE OXIDE-O) URANIUM(IV) P. CHARPIN, M.NIERLICH, G. CHEVRIER, D. VIGNER, M. LANCE, D. BAUDRY, *Acta Cryst., C(Cr. Str. Comm.)*, 1987(43), 1255
58	FIZZIX	BROMO-DI-IODO-BIS(TRIPHENYLPHOSPHINE OXIDE) THALLIUM(III) A. CASTINEIRAS, W. HILLER, J. STRAHLE, M.R. BERMEJO, M. GAYOSO, *An Quim., Ser. B*, 1986(82), 282
59	FLBZTL	BIS(μ-PENTAFLUOROBENZOATO)-BIS(BIS(PENTAFLUOROPHENYL)--(TRIPHENYLPHOSPHINE OXIDE) THALLIUM(III) K. HENRICK, M. MCPARTLIN, G.B. DEACON, R.J. PHILLIPS, *J. Organomet. Chem.*, 1981(204), 287
60	FOJFIT	DI-IODO-(μ-2--OXO)-TETRAOXO-(TRIPHENYLPHOSPHINE) TRIPHENYLPHOSPHINE OXIDE-O) DI-RHENIUM(V) BENZENE SOLVATE G. CIANI, A. SIRONI, T. BERINGHELLI, G. D'ALFONSO, M. FRENI, *Inorg. Chim. Acta*, 1986(113), 61
61	FUCHEQ	(OCTAETHYLPORPHINATO-N,N',N'',N''')-BIS(TRIPHENYLPHOSPHINE OXIDE) OSMIUM(II) TRIHYDRATE CHI-MING CHE, TING-FONG LAI, WAI-CHEUNG CHUNG, W.P. SCHAEFER, H.B. GRAY, *Inorg. Chem.*, 1987(26), 3907

No.	Ref. Code	Compoud Name Source Reference
62	GAVXUW	BIS(ACETYLACETONATO-O,O')-DICHLORO-TRIPHENYLPHOSPHINE OXIDE URANIUM(IV) TETRAHYDROFURAN SOLVATE C. BAUDIN, P. CHARPIN, M. EPHRITIKHINE, M. LANCE, M. NIERLICH, J. VIGNER, *J. Organomet. Chem.*, 1988(345), 263
63	GAVYAD	BIS(ACETYLACETONATO-O,O')-(ETA-5--CYCLOPENTADIENYL)-CHLORO--(TRIPHENYLPHOSPHINE)OXY URANIUM(IV) TETRAHYDROFURAN SOLVATE C. BAUDIN, P. CHARPIN, M. EPHRITIKHINE, M. LANCE, M. NIERLICH, J. VIGNER, *J. Organomet. Chem.*, 1988(345), 263
64	GEBSAH	BIS(BIS(μ-2--2-CHLOROPROPIONATO-O,O')-(TRIPHENYLPHOSPHINE OXIDE-O) COPPER(II) B. KOREN, P. SIVY, F. VALACH, M. MELNIK, J. JECNY, *Acta Cryst., C (Cr. Str. Comm.)*, 1987(28), 90-1
65	GEBYAN	TRIS(NITRATO-O,O')-BIS(TRIPHENYLPHOSPHINE OXIDE-O)-(ETHANOL-O) EUROPIUM(III) G. VALLE, G. CASOTTO, P.L. ZANONATO, B. ZARLI, *Polyhedron*, 1986(5), 2093
66	NPPOSO	DINITRATO-DIPHENYLYL(TRIPHENYLPHOSPHINE OXIDE) TIN(IV) M. NARDELLI, C. PELIZZI, G. PELIZZI, *J. Chem. Soc., Dalton*, 1978, 131
67	NTPOCE	TETRANITRATO-BIS(TRIPHENYLPHOSPHINE OXIDE) CERIUM(IV) M. -UL-HAQUE, C.N. CAUGHLAN, F.A. HART, R. VAN NICE, *Inorg. Chem.*, 1971(10), 115
68	QQQDEY01	DINITRATO-DIOXO-BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM(VI) N.W. ALCOCK, M.M. ROBERTS, D. BROWN, *J. Chem. Soc., Dalton*, 1982, 25
69	TAOTPU	BIS(DITHIOACETATO)-DIOXO-(TRIPHENYLPHOSPHINE OXIDE) URANIUM(VI) G. BOMBIERI, U. CROATTO, E. FORSELLINI, B. ZARLI, R. GRAZIANI, *J. Chem. Soc., Dalton*, 1972, 560
70	TCXPOM	TRICHLORO-OXO-BIS(TRIPHENYLPHOSPHINE OXIDE) MOLYBDENUM(V) C.D. GARNER, N.C. HOWLADER, F.E. MABBS, A.T. MCPHAIL, K.D. ONAN, *J. Chem. Soc., Dalton*, 1978, 1848

No.	Ref. Code	Compoud Name Source Reference
71	TFPOND	TRIS(THENOYL-TRIFLUOROACETONATO)-BIS(TRIPHENYLPHOSPHINE OXIDE) NEODYMIUM(III) J.G. LEIPOLDT, L.D.C. BOK, A.E. LAUBSCHER, S.S. BASSON, *J. Inorg. Nucl. Chem.*, 1975(37), 2477
72	TPOBII10	DI-μ-IODO-BIS(DI-IODO-BIS(TRIPHENYLPHOSPHINE OXIDE) BISMUTH(III) F. LAZARINI, S. MILICEV, *Acta Crystallogr., Sect. B,* 1976(32), 2873
73	TPOCLU10	TETRACHLORO-BIS(TRIPHENYLPHOSPHINE OXIDE) URANIUM(VI) G. BOMBIERI, D. BROWN, R. GRAZIANI, *J. Chem., Soc., Dalton,* 1975, 1873
74	TPPOSN	NITRATO-TRIPHENYL(TRIPHENYLPHOSPHINE OXIDE) TIN(IV) M. NARDELLI, C. PELIZZI, G. PELIZZI, *J. Organomet. Chem.*, 1976(112), 263

Table III.2: CSD Bibliographic Information On Trialkylphosphine Oxide Complexes

No.	Ref. Code	Compoud Name Source Reference
75	BIJXUN10	BIS(μ-2--DI-N-BUTYLPHOSPHATO-O,O')-BIS(NITRATO)-(TRI-N-BUTYLPHOSPHINE OXIDE)-DIOXO URANIUM(VI)) J.H. BURNS, *Inorg. Chem.*, 1983(22), 1174
76	CAMCUO	DIOXO-(TRIMETHYLPHOSPHINE OXIDE)-BIS(DIMETHYLPHOSPHINODITHIOATO) URANIUM A.E. STOREY, F. ZONNEVIJLLE, A.A. PINKERTON, D. SCHWARZENBACH, *Inorg. Chim., Acta,* 1983(75), 103
77	DOBMEM	TRIS(μ-2--ACETATO-O,O')-(μ-TRIETHYLPHOSPHONIUM--DITHIOCARBOXYLATO-S,S')-(TRIETHYLPHOSPHINE OXIDE-O)-DI-MOLYBDENUM TETRAFLUOROBORATE D.M. BAIRD, P.E. FANWICK, T. BAEWICK, *Inorg. Chem.*, 1985(24), 3753
78	FARZIH	DICHLORO-BIS(TRIMETHYLPHOSPHINE OXIDE) COBALT(II) F. EDELMANN, U. BEHRENS, *Acta Cryst., C (Cr. Str. Comm.),* 1986(42), 1715
79	ITMPOU	TETRAKIS(ISOTHIOCYANATO)-TETRAKIS(TRIMETHYLPHOSPHINE OXIDE) URANIUM(IV) C.E.F. RICKARD, D.C. WOOLLARD, *Aust. J. Chem.*, 1979(32), 2181
80	NOBPUR10	BIS(NITRATO)-BIS(TRI-N-BUTYLPHOSPHINE OXIDE)-DIOXO URANIUM(VI) J.H. BURNS, *Inorg. Chem.*, 1981(20), 3868
81	OXCLPC	μ-4--OXO-HEXA-μ-CHLORO-TETRAKIS(TRIETHYLPHOSPHINE OXIDE) COPPER(II)) M.R. CHURCHILL, B.G. DEBOER, S.J. MENDAK, *Inorg. Chem.*, 1975(14), 2496
82	PPNPOT	TETRAPHENYLPHOSPHONIUM PENTANITRATO-BIS(TRIMETHYLPHOSPHINE OXIDE) THORIUM(IV) N.W. ALCOCK, S. ESPERAS, K.W. BAGNALL, W. HSIAN-YUN, *J. Chem. Soc., Dalton,* 1978, 638
83	TMPOUC10	CHLORO-HEXAKIS(TRIMETHYLPHOSPHINE OXIDE) URANIUM(IV) TRICHLORIDE G. BOMBIERI, E. FORSELLINI, D. BROWN, B. WHITTAKER, *J. Chem. Soc., Dalton,* 1978, 638

Table III.3: CSD Bond distance Data On Triphenylphosphine Oxide Complexes

Note: Abbreviations and code numbers used in the table are explained on page 136

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
1	ACPOXU		U(VI)	1.481	2.375	1.773	1.812	1.788	0.064	4	0
2	AIXPOU	6	U(VI)	1.472 1.479	2.362 2.379	1.781 1.797	1.790 1.793	1.804 1.826	0.055	4	0
3	BEBHIZ	6	Np(VI)	1.502 1.502	2.363 2.363	1.791 1.791	1.802 1.802	1.803 1.803	0.049	3	0
4	BEBHUL		Np(VI)	1.498 1.547	2.288 2.261	1.970 1.777	1.807 1.841	1.774 1.646	0.042	2	0
5	BIJWEW	4	Zn(II)	1.507 1.507	1.966 1.966	1.825 1.825	1.764 1.764	1.796 1.796	0.043	3	0
6	BIJWIA	4	Zn(II)	1.524 1.486	1.964 1.970	1.792 1.803	1.794 1.813	1.769 1.800	0.042	4	0
7	BIRXIJ	4	Co(II)	1.476 1.476	1.990 1.990	1.786 1.786	1.788 1.788	1.764 1.764	0.063	3	0
8	BOFHIN	5	Cu(II)	1.452	1.948	1.832	1.832	1.832	0.054	3	0
9	BOMGAL	6	U(IV)	1.533 1.507	2.208 2.242	1.755 1.766	1.781 1.800	1.796 1.751	0.048	3	0
10	BOZWES	8	U(VI)	1.490	2.389	1.825	1.804	1.851	0.085	3	0
11	CACPOU		U(VI)	1.528	2.334	1.815	1.842	1.762	0.057	4	0
12	CADMAV		Re	1.503	2.092	1.779	1.765	1.778	0.039	3	0
13	CDXUPO	6	U(VI)	1.518 1.518	2.300 2.300	1.780 1.780	1.793 1.793	1.794 1.794	0.054	3	0

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
14	CECNUT		Os	1.492 1.528	2.001 1.940	1.885 1.655	1.768 1.788	1.719 1.809	0.076	0	0
15	CECYAK	5	Sn	1.510	2.335	1.800	1.803	1.805	0.055	3	0
16	CEKTAN	5	Th(III)	1.531 1.513	2.380 2.388	1.770 1.797	1.796 1.795	1.775 1.802	0.054	3	0
17	CEKTAN01	5	Th(III)	1.509 1.464	2.414 2.455	1.771 1.811	1.798 1.796	1.804 1.784	0.047	2	0
18	CFPOTL		Th(III)	1.480	2.392	1.812	1.798	1.804	0.044	3	0
19	CIWHIZ10	6	Sn(IV)	1.523 1.515	2.182 2.169	1.794 1.783	1.783 1.808	1.792 1.791	0.063	3	0
20	CLOPHW	6	W(V)	1.488 1.488	2.089 2.089	1.798 1.798	1.807 1.807	1.782 1.782	0.083	4	0
21	CLPHOV	5	V(V)	1.489 1.500	2.001 1.988	1.782 1.797	1.783 1.793	1.795 1.794	0.066	0	0
22	CLPOMN10	4	Mn(II)	1.512 1.508	2.020 2.109	1.830 1.796	1.751 1.798	1.823 1.820	0.079	3	0
23	CLPOZN	4	Zn(II)	1.497 1.497	1.983 1.983	1.797 1.797	1.805 1.805	1.816 1.816	0.076	0	0
24	CLTPOC01	4	Co(II)	1.505 1.505	1.940 1.940	1.803 1.803	1.798 1.798	1.791 1.791	0.049	3	0
25	COJYEF	6	Nb(V)	1.495 1.495	2.135 2.135	1.776 1.776	1.813 1.813	1.796 1.796	0.043	3	0
26	CONTEE		Mn(II)	1.498 1.485 1.498 1.485	2.084 2.147 2.084 2.147	1.785 1.794 1.785 1.794	1.798 1.798 1.798 1.798	1.790 1.808 1.790 1.808	0.050	0	0

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
27	CPPOCU01			1.518	1.879	1.792	1.792	1.792	0.084	4	0
28	CPPOCU02		Cu(II)	1.475	1.929	1.798	1.798	1.798	0.018	1	0
29	CTPOCU	4	Cu(II)	1.491 1.491	1.958 1.958	1.822 1.822	1.781 1.781	1.798 1.798	0.044	0	0
30	CTPOXB10	5	Sb(III)	1.503 1.503	2.455 2.455	1.797 1.797	1.797 1.797	1.799 1.799	0.027	0	0
31	CUPSEL		Sm	1.501 1.496	2.392 2.394	1.801 1.784	1.813 1.788	1.795 1.779	0.065	3	0
32	CUPSIP		Sm	1.514 1.495	2.356 2.391	1.809 1.806	1.801 1.807	1.815 1.778	0.051	3	0
33	CXPHOW	6	W(VI)	1.499 1.500	2.175 2.163	1.784 1.787	1.773 1.786	1.806 1.806	0.046	3	0
34	DALYAQ	6	U(VI)	1.506 1.481	2.307 2.377	1.786 1.786	1.780 1.719	1.767 1.828	0.070	4	0
35	DAPNEN	6	Sn	1.510 1.510	2.083 2.083	1.792 1.792	1.792 1.792	1.792 1.792	0.027	2	0
36	DBTPOC	4	Cu(II)	1.534 1.499	1.914 1.957	1.825 1.821	1.789 1.813	1.809 1.821	0.062	0	0
37	DEGGIF10	4	Mn(II)	1.487 1.487	2.069 2.069	1.796 1.796	1.808 1.808	1.788 1.788	0.046	3	0
38	DESREY	6	U(IV)	1.513 1.513	2.273 2.273	1.772 1.772	1.786 1.786	1.795 1.795	0.065	4	0
39	DEVYIM	4	Co(II)	1.522	1.917	1.794	1.789	1.781	0.033	0	0
40	DILWUQ		Cu(II)	1.477	2.097	1.794	1.803	1.794	0.047	2	0
41	DIRSOM	6	Sn	1.501 1.504	2.258 2.236	1.865 1.730	1.899 1.768	1.877 1.766	0.046	3	0

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
42	DOBMAI		Mo	1.485	2.390	1.779	1.783	1.790	0.051	3	0
43	DOLSUS	7	U	1.499 1.510	2.299 2.315	1.808 1.768	1.797 1.798	1.784 1.790	0.062	3	0
44	DOTDEV	7	Nd	1.496 1.487 1.495 1.502	2.388 2.423 2.379 2.350	1.783 1.808 1.785 1.802	1.810 1.808 1.807 1.779	1.799 1.771 1.809 1.818	0.055	3	0
45	DOWLIK	4	U(III)	1.491	2.389	1.794	1.799	1.796	0.025	3	0
46	DUHTIJ	6	Sn	1.474 1.491	2.148 2.119	1.832 1.795	1.790 1.783	1.769 1.816	0.050	3	0
47	DUHTOP	6	Sn	1.484 1.504	2.242 2.213	1.778 1.802	1.796 1.825	1.802 1.812	0.051	3	0
48	DUHVAD		Fe(II) & Fe(III)	1.496 1.473	2.007 2.019	1.812 1.812	1.770 1.812	1.796 1.767	0.074	3	0
49	DURDOJ	4	Cu(II)	1.509 1.509	1.941 1.941	1.797 1.797	1.799 1.799	1.801 1.801	0.050	0	0
50	DUVSOC	4	Pd(II)	1.500	2.109	1.790	1.831	1.789	0.054	3	0
51	DUZDOR	5	Th(III)	1.498 1.481	2.429 2.453	1.798 1.782	1.786 1.813	1.782 1.793	0.049	2	0
52	FABMUQ10		W(V)	1.518	2.125	1.777	1.788	1.802	0.062	3	0
53	FAKDUQ		Mn(III)	1.489	2.137	1.796	1.802	1.781	0.059	3	0
54	FELHAF	6	Sn	1.504 1.525	2.104 2.102	1.800 1.812	1.806 1.797	1.800 1.801	0.049	0	0
55	FICPUC		Th(IV)	1.512 1.507	2.367 2.367	1.812 1.789	1.814 1.815	1.803 1.797	0.027	3	0

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
56	FILCEI	6	Sn	1.503 1.526	2.230 2.264	1.874 1.791	1.804 1.780	1.795 1.857	0.082	0	0
57	FILFAH	6	U(IV)	1.514 1.525	2.335 2.233	1.780 1.785	1.724 1.866	1.779 1.812	0.040	4	0
58	FIZZIX	5	Tl(III)	1.512 1.505	2.423 2.451	1.793 1.786	1.869 1.825	1.836 1.819	0.067	0	0
59	FLBZTL		Tl(III)	1.488	2.375	1.831	1.782	1.798	0.045	3	0
60	FOJFIT		Re(V)	1.490	2.080	1.788	1.809	1.785	0.033	0	0
61	FUCHEQ		Os(II)	1.483 1.483	2.035 2.035	1.792 1.792	1.776 1.776	1.765 1.765	0.056	3	0
62	GAVXUW		U(IV)	1.493	2.325	1.750	1.808	1.801	0.046	4	0
63	GAVYAD		U	1.489	2.404	1.781	1.771	1.805	0.040	4	0
64	GEBSAH		Cu(II)	1.507	2.095	1.793	1.792	1.815	0.061	0	0
65	GEBYAN		Eu(III)	1.503 1.500	2.311 2.296	1.794 1.786	1.791 1.793	1.798 1.786	0.044	2	0
66	NPPOSO		Sn(IV)	1.487	2.148	1.806	1.765	1.819	0.059	3	0
67	NTPOCE	6	Ce(IV)	1.530	2.215	1.792	1.834	1.816	0.047	3	0
68	QQQDEY01	6	U(VI)	1.505 1.505	2.359 2.359	1.802 1.802	1.797 1.797	1.776 1.776	0.028	3	0
69	TAOTPU	5	U(VI)	1.473	2.334	1.799	1.765	1.831	0.056	3	0
70	TCXPOM	6	Mo(V)	1.516 1.506 1.502 1.489	2.135 2.066 2.115 2.107	1.777 1.735 1.791 1.806	1.759 1.801 1.776 1.762	1.795 1.771 1.788 1.769	0.067	0	0
71	TFPOND	5	Nd(III)	1.500 1.491	2.396 2.422	1.802 1.828	1.799 1.803	1.796 1.793	0.084	0	0

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
72	TPOBII10		Bi(III)	1.508 1.499	2.481 2.402	1.798 1.805	1.811 1.807	1.803 1.803	0.033	2	0
73	TPOCLU10	5	U(IV)	1.524 1.524	2.243 2.243	1.778 1.778	1.825 1.825	1.786 1.786	0.047	3	0
74	TPPOSN		Sn(IV)	1.471	2.289	1.792	1.830	1.796	0.064	4	0

Table III.4: CSD Bond distance Data On Trialkylphosphine Oxide Complexes

Note: Abbreviations and code numbers used in the table are explained on page 136

No.	Ref. Code	CN	M	Bond Distances					RF	AS	ERR.
				P-O	M-O	P-C1	P-C2	P-C3			
75	BIJXUN10	7	U(VI)	1.520	2.298	1.801	1.773	1.818	0.052	4	0
76	CAMCUO	7	U	1.446	2.318	1.811	1.939	1.939	0.050	3	0
77	DOBMEM	6	Mo	1.502	2.348	1.806	1.811	1.797	0.046	2	0
78	FARZIH	4	Co(II)	1.508	1.958	1.769	1.775	1.771	0.044	0	0
				1.508	1.962	1.779	1.756	1.777			
79	ITMPOU	8	U(IV)	1.463	2.326	1.803	1.815	1.807	0.040	4	0
				1.463	2.326	1.803	1.815	1.807			
80	NOBPUR10	7	U(VI)	1.489	2.347	1.851	1.769	1.733	0.043	3	0
				1.489	2.347	1.851	1.769	1.733			
81	OXCLPC	5	Cu(II)	1.392	1.935	1.727	1.727	1.727	0.036	0	0
				1.503	1.933	1.775	1.820	1.759			
82	PPNPOT	12	Th(IV)	1.485	2.421	1.793	1.830	1.830	0.054	0	0
				1.491	2.339	1.758	1.818	1.818			
83	TMPOUC10	7	U(IV)	1.513	2.251	1.777	1.812	1.774	0.023	0	0
				1.535	2.272	1.762	1.801	1.817			
				1.513	2.251	1.777	1.812	1.774			
				1.513	2.251	1.777	1.812	1.774			
				1.535	2.272	1.762	1.801	1.817			
				1.535	2.272	1.762	1.801	1.817			

Table III.5: CSD Bond Angles Data On Triphenylphosphine Oxide Complexes

Note: Abbreviations and code numbers used in the table are explained on page 136

No.	Ref. Code	CN	M	Bond Angles							RF	AS	ERR.
				MOP	OPC1	OPC2	OPC3	C1PC2	C1PC3	C2PC3			
1	ACPOXU		U(VI)	167.9	110.2	110.5	112.4	106.4	109.1	108.1	0.064	4	0
2	AIXPOU	6	U(VI)	166.3	110.7	110.9	109.6	109.2	108.7	107.7	0.055	4	0
				143.3	113.2	109.1	111.9	108.8	108.1	105.4			
3	BEBHIZ	6	Np(VI)	159.1	112.8	111.1	109.2	110.4	107.1	106.1	0.049	3	0
				159.1	112.8	111.1	109.2	110.4	107.1	106.1			
4	BEBHUL		Np(VI)	167.2	114.3	110.7	110.2	105.2	105.7	110.6	0.042	2	0
				152.8	110.9	111.8	107.8	108.8	104.4	112.8			
5	BIJWEW	4	Zn(II)	154.1	110.0	109.8	112.9	110.7	105.1	108.2	0.043	3	0
				154.1	110.0	109.8	112.9	110.7	105.1	108.2			
6	BIJWIA	4	Zn(II)	145.1	111.4	106.7	112.7	107.5	111.0	107.3	0.042	4	0
				157.0	113.8	111.3	110.3	106.7	107.8	106.7			
7	BIRXIJ	4	Co(II)	158.5	111.5	107.7	113.3	109.1	105.8	109.5	0.063	3	0
				158.5	111.5	107.7	113.3	109.1	105.8	109.5			
8	BOFHIN	5	Cu(II)	180.0	111.4	111.4	111.4	107.5	107.5	107.5	0.054	3	0
9	BOMGAL	6	U(IV)	167.6	109.4	108.0	109.2	112.2	110.0	107.8	0.048	3	0
				160.0	109.5	109.0	109.6	107.6	110.9	110.2			
10	BOZWES	8	U(VI)	150.8	111.7	113.1	109.5	108.7	105.4	108.2	0.085	3	0
11	CACPOU		U(VI)	157.9	112.8	108.7	111.2	107.9	106.2	110.0	0.057	4	0
12	CADMAV		Re	148.7	115.3	106.8	110.1	107.4	108.0	109.2	0.039	3	0
13	CDXUPO	6	U(VI)	158.7	110.9	109.4	111.7	108.9	108.3	107.6	0.054	3	0
				158.7	110.9	109.4	111.7	108.9	108.3	107.6			

No.	Ref. Code	CN	M	Bond Angles MOP OPC1 OPC2 OPC3 C1PC2 C1PC3 C2PC3	RF	AS	ERR.
14	CECNUT		Os	148.1 110.5 109.6 114.3 107.4 107.6 107.2 158.0 107.9 110.1 110.8 104.3 114.1 109.6	0.076	0	0
15	CECYAK	5	Sn	146.9 110.0 112.4 109.8 109.7 105.8 108.9	0.055	3	0
16	CEKTAN	5	Th(III)	151.8 111.4 111.0 112.2 107.6 107.2 107.3 150.4 114.7 109.7 110.7 107.7 106.6 107.2	0.054	3	0
17	CEKTAN01	5	Th(III)	149.2 112.9 108.9 113.5 107.7 106.8 106.7 147.8 108.2 111.1 115.9 105.7 107.7 107.7	0.047	2	0
18	CFPOTL		Th(III)	168.0 110.9 111.7 108.9 107.6 107.4 110.3	0.044	3	0
19	CIWHIZ10	6	Sn(IV)	148.3 108.3 112.8 113.0 105.6 107.3 109.5 158.3 113.2 110.4 109.8 106.5 110.3 106.3	0.063	3	0
20	CLOPHW	6	W(V)	159.9 112.7 108.5 111.3 106.3 109.0 108.9 159.9 112.7 108.5 111.3 106.3 109.0 108.9	0.083	4	0
21	CLPHOV	5	V(V)	159.5 109.9 112.7 109.9 106.0 109.2 109.0 146.2 109.4 113.7 109.5 106.5 109.6 108.1	0.066	0	0
22	CLPOMN10	4	Mn(II)	160.8 111.1 112.1 111.9 108.9 105.6 107.0 155.6 113.6 110.5 112.0 105.7 107.2 107.6	0.079	3	0
23	CLPOZN	4	Zn(II)	153.4 111.4 108.8 112.9 110.0 106.0 107.8 153.4 111.4 108.8 112.9 110.0 106.0 107.8	0.076	0	0
24	CLTPOC01	4	Co(II)	155.2 111.6 113.2 108.5 105.4 110.2 107.9 155.2 111.6 113.2 108.5 105.4 110.2 107.9	0.049	3	0
25	COJYEF	6	Nb(V)	162.0 112.7 109.4 111.3 107.7 107.1 108.6 162.0 112.7 109.4 111.3 107.7 107.1 108.6	0.043	3	0
26	CONTEE		Mn(II)	167.5 110.3 113.0 112.3 107.7 107.9 105.3 162.7 112.3 110.8 111.4 109.5 106.9 105.7 167.5 110.3 113.0 112.3 107.7 107.9 105.3 162.7 112.3 110.8 111.4 109.5 106.9 105.7	0.050	0	0
27	CPPOCU01		Cu(II)	180.0 111.6 111.6 111.6 107.3 107.3 107.3	0.084	4	0

No.	Ref. Code	CN	M	Bond Angles MOP OPC1 OPC2 OPC3 C1PC2 C1PC3 C2PC3	RF	AS	ERR.
28	CPPOCU02		Cu(II)	180.0 111.5 111.5 111.5 107.5 107.5 107.5	0.084	4	0
29	CTPOCU	4	Cu(II)	150.9 111.8 108.5 113.5 110.3 105.5 107.2 150.9 111.8 108.5 113.5 110.3 105.5 107.2	0.044	0	0
30	CTPOXB10	5	Sb(III)	141.1 110.1 110.5 112.6 106.9 107.5 109.0 141.1 110.1 110.5 112.6 106.9 107.5 109.0	0.027	0	0
31	CUPSEL		Sm	167.6 113.4 112.3 111.2 105.4 105.3 108.9 168.8 114.4 110.7 112.1 106.0 104.2 109.1	0.065	3	0
32	CUPSIP		Sm	163.0 113.1 112.4 110.1 106.9 105.3 108.7 158.8 110.1 112.3 112.9 105.1 108.6 107.6	0.051	3	0
33	CXPHOW	6	W(VI)	159.0 109.7 113.1 111.3 108.0 106.3 108.1 165.5 108.1 116.3 110.5 107.0 107.7 107.0	0.046	3	0
34	DALYAQ	6	U(VI)	163.0 113.9 110.8 114.5 107.8 101.8 107.3 154.1 107.3 112.4 112.2 105.1 113.2 106.5	0.070	4	0
35	DAPNEN	6	Sn	157.2 107.9 111.8 113.8 109.1 107.4 106.8 157.2 107.9 111.8 113.8 109.1 107.4 106.8	0.027	2	0
36	DBTPOC	4	Cu(II)	144.0 113.2 113.8 107.5 108.5 103.9 109.4 154.8 111.5 111.0 112.1 108.6 106.2 107.3	0.062	0	0
37	DEGGIF10	4	Mn(II)	156.1 112.8 109.0 111.5 107.6 106.3 109.6 156.1 112.8 109.0 111.5 107.6 106.3 109.6	0.046	3	0
38	DESREY	6	U(IV)	170.9 109.8 109.8 111.5 108.8 109.3 107.7 170.9 109.8 109.8 111.5 108.8 109.3 107.7	0.065	4	0
39	DEVYIM	4	Co(II)	137.6 109.9 106.4 112.5 108.6 110.1 109.2	0.033	0	0
40	DILWUQ		Cu(II)	149.0 109.4 114.2 111.1 108.7 108.2 105.1	0.047	2	0
41	DIRSOM	6	Sn	172.5 114.1 104.5 108.8 111.2 110.3 107.6 174.7 118.1 106.8 111.3 106.8 108.5 104.3	0.046	3	0
42	DOBMAI		Mo	142.3 111.8 109.7 113.4 108.3 106.0 107.4	0.051	3	0

No.	Ref. Code	CN	M	Bond Angles MOP OPC1 OPC2 OPC3 C1PC2 C1PC3 C2PC3	RF	AS	ERR.
43	DOLSUS	7	U	148.6 109.5 109.4 113.3 109.8 107.2 107.6 166.4 111.3 110.2 109.9 108.0 107.8 109.6	0.062	3	0
44	DOTDEV	7	Nd	153.3 112.2 109.8 111.2 107.4 108.6 107.6 170.2 112.0 110.0 113.9 109.3 105.2 106.3 173.6 110.8 111.5 112.1 108.7 106.6 106.8 158.5 112.7 111.5 110.5 109.2 109.0 103.6	0.055	3	0
45	DOWLIK	4	U(III)	162.8 110.3 110.5 112.0 107.1 109.7 107.0	0.025	3	0
46	DUHTIJ	6	Sn	152.0 111.1 113.4 108.7 110.0 107.9 105.5 163.7 111.6 108.6 111.4 105.6 110.8 108.6	0.050	3	0
47	DUHTOP	6	Sn	155.7 114.6 111.2 107.9 106.6 110.1 106.2 159.3 113.2 108.0 112.7 108.9 108.9 104.9	0.051	3	0
48	DUHVAD		Fe(II) & Fe(III)	160.4 113.5 111.5 110.6 107.1 107.4 106.3 155.8 112.9 107.6 110.3 108.5 108.3 109.1	0.074	3	0
49	DURDOJ	4	Cu(II)	140.4 113.6 107.3 111.3 107.2 108.9 108.4 140.4 113.6 107.3 111.3 107.2 108.9 108.4	0.050	0	0
50	DUVSOC	4	Pd(II)	132.1 115.8 110.4 109.5 106.0 106.4 108.4	0.054	3	0
51	DUZDOR	5	Th(III)	150.7 112.7 110.4 111.6 107.1 106.6 108.2 148.2 109.5 110.0 116.1 107.3 106.7 107.0	0.049	2	0
52	FABMUQ10		W(V)	155.8 112.2 110.6 112.0 106.4 107.2 108.3	0.062	3	0
53	FAKDUQ		Mn(III)	163.5 110.8 109.1 112.7 109.3 106.7 108.1	0.059	3	0
54	FELHAF	6	Sn	160.2 108.0 113.2 111.1 107.8 109.5 107.3 151.8 110.6 107.9 113.7 106.9 109.9 107.6	0.049	0	0
55	FICPUC		Tn(IV)	173.0 110.6 110.5 112.8 106.9 106.9 108.9 169.0 110.6 112.1 111.0 107.5 107.7 107.7	0.027	3	0
56	FILCEI	6	Sn	157.8 112.2 108.1 110.6 108.4 110.6 106.7 157.9 111.5 109.9 112.1 109.3 104.9 109.1	0.082	0	0

No.	Ref. Code	CN	M	Bond Angles MOP OPC1 OPC2 OPC3 C1PC2 C1PC3 C2PC3	RF	AS	ERR.
57	FILFAH	6	U(IV)	155.4 107.4 111.3 112.6 108.2 106.8 110.3 167.8 109.1 109.9 110.4 111.1 107.9 108.4	0.040	4	0
58	FIZZIX	5	Th(III)	151.8 112.1 112.6 110.6 106.7 108.3 106.1 147.2 110.6 110.5 116.8 107.0 105.9 105.5	0.067	0	0
59	FLBZTL		Th(III)	150.5 108.2 112.3 111.1 108.9 108.5 107.8	0.045	3	0
60	FOJFIT		Re(V)	151.3 111.7 108.7 109.9 107.0 108.5 111.0	0.033	0	0
61	FUCHEQ		Os(II)	154.2 107.9 115.0 108.8 106.8 111.2 107.2 154.2 107.9 115.0 108.8 106.8 111.2 107.2	0.056	3	0
62	GAVXUW		U(IV)	160.4 108.6 109.3 113.0 108.5 111.2 106.3	0.046	4	0
63	GAVYAD		U	160.0 110.8 111.3 114.0 104.7 109.8 105.6	0.040	4	0
64	GEBSAH		Cu(II)	146.7 110.0 114.8 111.0 106.8 107.1 106.8	0.061	0	0
65	GEBYAN		Eu(III)	163.8 111.0 110.4 113.1 107.5 107.4 107.3 168.2 112.9 110.7 109.8 107.9 107.5 107.9	0.044	2	0
66	NPPOSO		Sn(IV)	162.5 108.6 113.3 109.7 107.8 109.5 108.0	0.059	3	0
67	NTPOCE	6	Ce(IV)	169.2 107.3 110.3 112.3 109.4 110.6 107.0	0.047	3	0
68	QQQDEY01	6	U(VI)	160.0 112.5 111.2 109.7 109.4 107.2 106.6 160.0 112.5 111.2 109.7 109.4 107.2 106.6	0.028	3	0
69	TAOTPU	5	U(VI)	159.4 113.9 109.6 109.0 107.9 107.7 108.7	0.056	3	0
70	TCXPOM	6	Mo(V)	168.6 110.7 110.6 111.2 109.2 107.7 107.3 145.6 111.5 106.3 112.2 111.0 106.7 109.2 164.9 110.2 108.2 111.4 107.3 108.1 111.5 165.3 110.2 107.8 112.0 110.0 106.4 110.4	0.067	0	0
71	TFPOND	5	Nd(III)	171.4 112.1 111.8 109.8 107.2 106.9 108.9 161.0 112.9 111.6 111.7 104.4 108.5 107.4	0.084	0	0
72	TPOBII10		Bi(III)	154.4 112.8 109.9 111.8 107.7 107.6 106.7 176.2 111.6 112.4 110.6 106.6 108.0 107.6	0.033	2	0

No.	Ref. Code	CN	M	Bond Angles MOP OPC1 OPC2 OPC3 C1PC2 C1PC3 C2PC3	RF	AS	ERR.
73	TPOCLU10	5	U(IV)	165.1 109.5 110.3 110.2 109.4 109.3 108.1 165.1 109.5 110.3 110.2 109.4 109.3 108.1	0.047	3	0
74	TPPOSN		Sn(IV)	152.5 111.3 114.3 110.5 105.7 108.0 106.6	0.064	4	0

Table III.6: CSD Bond Angles Data On Trialkylphosphine Oxide Complexes

Note: Abbreviations and code numbers used in the table are explained on page 136

No.	Ref. Code	CN	M	Bond Angles MOP OPC1 OPC2 OPC3 C1PC2 C1PC3 C2PC3	RF	AS	ERR.
75	BIJXUN10	7	U(VI)	148.4 110.8 110.0 112.1 112.4 101.2 110.1	0.052	4	0
76	CAMCUO	7	U	163.0 104.0 106.6 106.6 109.5 109.5 119.4	0.050	3	0
77	DOBMEM	6	Mo	144.9 111.0 112.2 110.3 105.0 109.9 108.3	0.046	2	0
78	FARZIH	4	Co(II)	131.5 111.6 110.2 111.9 107.7 108.3 106.8 131.6 111.4 110.9 111.2 107.2 108.5 107.5	0.044	0	0
79	ITMPOU	8	U(IV)	153.6 111.0 112.0 111.0 106.7 107.8 108.1 153.6 111.0 112.0 111.0 106.7 107.8 108.1	0.040	4	0
80	NOBPUR10	7	U(VI)	146.0 109.5 109.0 111.6 108.0 108.2 110.5 146.0 109.5 109.0 111.6 108.0 108.2 110.5	0.043	3	0
81	OXCLPC	5	Cu(II)	180.0 115.0 115.0 115.0 103.5 103.5 103.5 141.0 109.9 110.4 111.3 101.8 112.1 111.0	0.036	0	0
82	PPNPOT	12	Th(IV)	152.7 113.2 111.7 111.7 104.0 104.0 111.9 169.0 112.4 110.6 110.6 105.7 105.7 111.8	0.054	0	0
83	TMPOUC10	7	U(IV)	152.1 109.2 110.2 111.8 108.8 108.7 108.2 146.8 110.3 111.3 110.2 108.1 108.2 108.6 152.1 109.2 110.2 111.8 108.8 108.7 108.2 152.1 109.2 110.2 111.8 108.8 108.7 108.2 146.8 110.3 111.3 110.2 108.1 108.2 108.6 146.8 110.3 111.3 110.2 108.1 108.2 108.6	0.023	0	0

Table III.7: CSD Bond Torsions Data On Triphenylphosphine Oxide Complexes

Note: Abbreviations and code numbers used in the table are explained on page 136

No.	Ref. Code	CN	M	Torsion Angle			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
1	ACPOXU		U(VI)	50.8	168.1	-71.1	0.064	4	0
2	AIXPOU	6	U(VI)	-140.7 12.9	-19.4 134.3	99.4 -109.5	0.055	4	0
3	BEBHIZ	6	Np(VI)	-84.5 84.5	40.1 -40.1	156.6 -156.6	0.049	3	0
4	BEBHUL		Np(VI)	152.7 -138.3	-88.8 -16.7	33.9 108.0	0.042	2	0
5	BIJWEW	4	Zn(II)	64.5 64.5	-173.5 -173.5	-52.6 -52.6	0.043	3	0
6	BIJWIA	4	Zn(II)	45.4 -38.4	162.4 -159.0	-80.2 82.8	0.042	4	0
7	BIRXIJ	4	Co(II)	-65.5 -65.5	174.9 174.9	53.7 53.7	0.063	3	0
8	BOFHIN	5	Cu(II)	-90.0	-90.0	90.0	0.054	3	0
9	BOMGAL	6	U(IV)	-136.5 83.1	101.0 -159.4	-16.0 -38.8	0.048	3	0
10	BOZWES	8	U(VI)	82.0	-40.9	-161.7	0.085	3	0
11	CACPOU		U(VI)	74.8	-165.7	-44.5	0.057	4	0
12	CADMAV		Re	29.0	148.2	-93.4	0.039	3	0
13	CDXUPO	6	U(VI)	-93.3 93.3	146.6 -146.6	27.6 -27.6	0.054	3	0

No.	Ref. Code	CN	M	Torsion Angle			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
14	CECNUT		Os	141.1 125.2	-100.8 12.0	19.6 -109.4	0.076	0	0
15	CECYAK	5	Sn	-123.0	-0.5	121.0	0.055	3	0
16	CEKTAN	5	Th(III)	163.8 20.5	43.9 141.8	-76.1 -100.1	0.054	3	0
17	CEKTAN01	5	Th(III)	-44.5 -143.0	-164.0 101.3	77.3 -22.0	0.047	2	0
18	CFPOTL		Th(III)	85.9	-34.1	-156.1	0.044	3	0
19	CIWHIZ10	6	Sn(IV)	167.6 -5.0	51.1 -124.4	-73.7 118.7	0.063	3	0
20	CLOPHW	6	W(V)	-34.2 -34.2	-151.6 -151.6	88.6 88.6	0.083	4	0
21	CLPHOV	5	V(V)	-150.3 110.6	-32.3 -8.3	89.5 -129.4	0.066	0	0
22	CLPOMN10	4	Mn(II)	142.7 -6.7	-95.2 -125.2	25.0 114.9	0.079	3	0
23	CLPOZN	4	Zn(II)	-64.4 -64.4	174.2 174.2	54.7 54.7	0.076	0	0
24	CLTPOC01	4	Co(II)	-64.5 -64.5	54.1 54.1	173.9 173.9	0.049	3	0
25	COJYEF	6	Nb(V)	-28.7 -28.7	-148.5 -148.5	91.6 91.6	0.043	3	0
26	CONTEE		Mn(II)	-173.4 -62.2 173.4 62.2	-52.8 60.5 52.8 -60.5	66.1 177.8 -66.1 -177.8	0.050	0	0
27	CPPOCU01		Cu(II)	-90.0	-90.0	90.0	0.084	4	0

No.	Ref. Code	CN	M	Torsion Angle			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
28	CPPOCU02		Cu(II)	-90.0	-90.0	90.0	0.018	1	0
29	CTPOCU	4	Cu(II)	51.0 51.0	172.9 172.9	-68.1 -68.1	0.044	0	0
30	CTPOXB10	5	Sb(III)	-137.3 -137.3	104.8 104.8	-17.3 -17.3	0.027	0	0
31	CUPSEL		Sm	-116.0 -102.7	3.3 137.7	125.6 15.7	0.065	3	0
32	CUPSIP		Sm	85.1 152.0	-36.0 -91.3	-157.4 30.5	0.051	3	0
33	CXPHOW	6	W(VI)	121.9 158.9	1.22 -38.7	-120.8 83.4	0.046	3	0
34	DALYAQ	6	U(VI)	-150.3 176.9	88.0 -68.1	-33.6 51.9	0.070	4	0
35	DAPNEN	6	Sn	154.9 154.9	-85.2 -85.2	35.9 35.9	0.027	2	0
36	DBTPOC	4	Cu(II)	-52.2 25.1	72.3 146.2	-166.3 -93.8	0.062	0	0
37	DEGGIF10	4	Mn(II)	56.8 56.8	176.1 176.1	-62.8 -62.8	0.046	3	0
38	DESREY	6	U(IV)	135.3 -135.3	-105.1 105.1	14.2 -14.2	0.065	4	0
39	DEVYIM	4	Co(II)	-93.2	149.5	29.9	0.033	0	0
40	DILWUQ		Cu(II)	-155.7	-33.6	85.0	0.047	2	0
41	DIRSOM	6	Sn	-71.1 -56.5	167.3 -176.8	52.5 70.0	0.046	3	0
42	DOBMAI		Mo	-84.0	155.8	35.8	0.051	3	0

No.	Ref. Code	CN	M	Torsion Angles			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
43	DOLSUS	7	U	-104.6 -46.6	135.0 73.2	15.0 -166.0	0.062	3	0
44	DOTDEV	7	Nd	-37.8 8.2 74.2 -91.8	-157.1 129.8 -47.1 145.0	84.0 -111.1 -166.8 30.4	0.055	3	0
45	DOWLIK	4	U(III)	105.6	-136.1	-16.9	0.025	3	0
46	DUHTIJ	6	Sn	39.2 -44.8	-85.3 -160.8	157.8 79.6	0.050	3	0
47	DUHTOP	6	Sn	-7.1 70.9	113.9 -168.5	-130.1 -53.2	0.051	3	0
48	DUHVAD		Fe(II) & Fe(III)	0.0 98.3	121.1 -25.9	-120.8 -140.1	0.074	3	0
49	DURDOJ	4	Cu(II)	-68.0 68.0	173.8 -173.8	55.4 -55.4	0.050	0	0
50	DUVSOC	4	Pd(II)	-2.5	117.9	-122.7	0.054	3	0
51	DUZDOR	5	Th(III)	-40.0 -135.5	-159.8 106.9	80.0 -14.8	0.049	2	0
52	FABMUQ10		W(V)	-87.1	154.4	33.5	0.062	3	0
53	FAKDUQ		Mn(III)	7.9	-112.4	127.4	0.059	3	
54	FELHAF	6	Sn	152.7 -85.4	33.5 158.0	-87.3 38.0	0.049	0	0
55	FICPUC		Tn(IV)	178.9 -62.6	60.7 57.4	-61.4 177.8	0.027	3	0
56	FILCEI	6	Sn	-77.5 -123.4	163.1 115.3	46.6 -6.2	0.082	0	0

No.	Ref. Code	CN	M	Torsion Angles			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
57	FILFAH	6	U(IV)	152.7 -121.8	-89.1 0.3	35.4 119.8	0.040	4	0
58	FIZZIX	5	Th(III)	-36.5 -134.5	-157.0 107.2	84.5 -13.3	0.067	0	0
59	FLBZTL		Th(III)	-152.4	-32.1	88.6	0.045	3	0
60	FOJFIT		Re(V)	78.1	-164.0	-42.3	0.033	0	0
61	FUCHEQ		Os(II)	-123.0 123.0	-4.1 4.1	116.2 -116.2	0.056	3	0
62	GAVXUW		U(IV)	85.6	-156.3	-38.2	0.046	4	0
63	GAVYAD		U	161.2	-82.8	36.6	0.040	4	0
64	GEBSAH		Cu(II)	-153.7	-33.3	88.0	0.061	0	0
65	GEBYAN		Eu(III)	-83.1 -19.0	157.9 102.1	37.7 -138.9	0.044	2	0
66	NPPOSO		Sn(IV)	160.2	40.5	-80.2	0.059	3	0
67	NTPOCE	6	Ce(IV)	-138.5	102.4	-16.7	0.047	3	0
68	QQQDEY01	6	U(VI)	-84.3 84.3	38.8 -38.8	156.5 -156.5	0.028	3	0
69	TAOTPU	5	U(VI)	-27.2	93.7	-147.4	0.056	3	0
70	TCXPOM	6	Mo(V)	-48.2 109.3 -53.9 130.9	-169.4 -129.6 -170.9 -109.0	71.5 -10.3 66.1 12.6	0.067	0	0
71	TFPOND	5	Nd(III)	0.7 -38.8	121.0 -156.0	-118.0 83.8	0.084	0	0
72	TPOBII10		Bi(III)	-27.1 -75.2	-147.3 44.4	94.4 164.6	0.033	2	0

No.	Ref. Code	CN	M	Torsion Angles			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
73	TPOCLU10	5	U(IV)	-156.9 -156.9	-36.5 -36.5	82.9 82.9	0.047	3	0
74	TPPOSN		Sn(IV)	-126.1	-6.4	113.9	0.064	4	0

Table III.8: CSD Bond Torsions Data On Triphenylphosphine Oxide Complexes

Note: Abbreviations and code numbers used in the table are explained on page 136

No.	Ref. Code	CN	M	Torsion Angles			RF	AS	ERR.
				MOPC1	MOPC2	MOPC3			
75	BIJXUN10	7	U(VI)	120.7	-4.2	-127.1	0.052	4	0
76	CAMCUO	7	U	180.0	-64.3	64.3	0.050	3	0
77	DOBMEM	6	Mo	98.6	-144.3	-23.4	0.046	2	0
78	FARZIH	4	Co(II)	92.5	-147.9	-29.2	0.044	0	0
				74.2	-146.5	-47.0			
79	ITMPOU	8	U(IV)	67.3	-173.5	-52.6	0.040	4	0
				67.3	-173.5	-52.6			
80	NOBPUR10	7	U(VI)	-17.9	100.1	-137.6	0.043	3	0
				-17.9	100.1	-137.6			
81	OXCLPC	5	Cu(II)	-90.0	90.0	-90.0	0.036	0	0
				125.0	-123.5	0.2			
82	PPNPOT	12	Th(IV)	-180.0	63.1	-63.1	0.054	0	0
				0.0	-117.8	117.8			
83	TMPOUC10	7	U(IV)	147.1	-93.5	26.9	0.023	0	0
				151.7	-88.3	32.3			
				147.1	-93.5	26.9			
				147.1	-93.5	26.9			
				151.7	-88.3	32.3			
				151.7	-88.3	32.3			

APPENDIX IV: ENERGY ACCOMPANYING COMPLEX FORMATION

IV.A CALCULATION METHOD

We assumed the following reaction for the formation of the tetrahedral zinc complex:

$$ZnCl_2 + 2R_3PO \rightleftharpoons ZnCl_2(R_3PO)_2$$

where

R = alkyl or phenyl ligand

The energy accompanying formation of the complex was calculated from the following relationship:

$$E_{complexation} = E_{complex} - [\,(2E_{ligand}) + E(ZnCl_2)\,] \qquad .....(4.5)$$

where

$E_{complexation}$ = Energy accompanying complex formation (complexation energy)

$E_{complex}$ = Energy for the isolated complex molecule

E_{ligand} = Energy for the isolated ligand molecule

$E\,(ZnCl_2)$ = Energy for $ZnCl_2$

Using Tables 4.9 and 4.10 on pages 76 and 77 (and taking the energy of $ZnCl_2$ as zero for simplicity), the energies accompanying complex formation were calculated with the aid of equation 4.5; these calculated complexation energies are summarised in Table IV.1.

Table IV.1: Calculated Complexation Energies For Tetrahedral $ZnCl_2L_2$ Complexes

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

ENERGY TERM	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
	STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
	TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TiPO	TSBPO	TPOPO	TPPO
$E_{COMPLEXATION}$	-10.6	-6.0	-10.7	-26.5	-14.6	-18.3	-18.3	-24.1	-19.9	-14.4	5.1	-13.1

V.B ANALYSIS OF CALCULATED COMPLEXATION ENERGIES

Generally speaking, Table IV.1 shows that straight chain ligands with longer carbon chains (TBPO, THPO and TOPO) have a more favourable energy of complexation than those with shorter carbon chain lengths (TMPO, TEPO and TNPPO). This is in contrast to changes in steric effects whereby the unsolvated ligands and complexes show increasing steric energy as the carbon chain length of straight chain ligands increases (Tables 4.8, 4.9 and 4.10). Also, Table IV.1 above show that branched chain systems generally have a favourable complexation energy. Furthermore, TPPO and TPOPO show the most unfavourable complexation energy among the branched chain systems, with TPOPO showing a very unfavourable positive complexation energy (Table IV.1).

To investigate the reason behind the complexation energy trends, we calculated the changes in all the energy terms accompanying complex formation in the same way as we did in calculating the changes in the total steric energy accompanying complex formation. These changes in energy terms accompanying complex formation are summarised in Table IV.2.

Table IV.2: Calculated Changes In The Energy Terms Accompanying Formation Of Tetrahedral $ZnCl_2L_2$ Complexes

(L = Trialkyl- or Triphenyl- phosphine oxide ligand)

ENERGY TERM	LIGAND TYPES (L) AND ENERGIES (energies in kcal/mole)											
	STRAIGHT CHAIN LIGANDS						BRANCHED CHAIN LIGANDS					
	TMPO	TEPO	TNPPO	TBPO	THPO	TOPO	TSPPO	TTPO	TIPO	TSBPO	TPOPO	TPPO
VDW	-4.0	-6.7	-7.8	-6.6	-6.9	-11.6	-7.8	-5.2	-9.2	-2.9	-5.9	-11.1
ELECT.	-7.0	-5.9	-7.0	-10.8	-10.2	-12.4	-16.1	-26.3	-12.6	-20.9	-4.0	-12.8
BONDS	0.1	0.4	0.0	-0.3	-0.8	0.7	0.4	1.1	-0.2	1.3	1.5	-0.4
ANGLES	0.3	2.8	1.9	-6.8	1.1	2.0	4.6	4.3	-2.6	4.8	13.4	5.9
TORSIONS	0.2	3.2	2.2	-1.8	2.6	3.0	0.6	2.0	4.6	3.3	0.0	5.2

Table IV.2 show that the major energy change on complex formation comes from the electrostatic and Van der Waals energy terms. This accounts for the observation that the trend in complexation energy generally follows the trend in the relative electrostatic and Van der Waals energies of the complex versus that of its ligands. The favourable electrostatic energy of the complex relative to that of its $ZnCl_2$ and ligand components may arise because the additional charged zinc metal and chloride ligands in the molecular system of the complex allow more favourable electrostatic interactions in the system (see earlier definition of 'a favourable charge distribution' on pages 86 and 87). This being the case, we should then expect different complexation energies for a range of metal complexes which only differ in the charge on the metal. What this implies is that the charge at the metal center can also be important in determining the ligand selectivity for metals of different charges. This claim will of course need more data for a more definitive conclusion. As for the favourable Van der Waals energy of the complex relative to that of its $ZnCl_2$ and ligand components, this may arise because of the additional favourable interligand Van der Waals interactions in the complex as opposed to the case of an isolated ligand where only intraligand Van der Waals interactions are occuring.

The positive complexation energy for TPOPO implies that formation of complexes involving TPOPO ligand is less favourable. This contradicts the fact that TPOPO (CYANEX 925) is a good extractant which is even available on a commercial scale (2). The contradiction may have occured due to the fact that our calculations does not take into

account the energy of formation for the unstrained bonds. The many bonds in the molecule is one indication that this formation energy could be favourable enough to offset the unfavourable steric energy in the molecule. It is also likely that the limited capabilities of the modeling program may not have been able to accurately reproduce the steric effects in the large and highly branched TPOPO ligand. This limitation may be deduced from Table IV.2 where, unlike for most other systems in Table IV.2, TPOPO angle energy term show an exceptionally unfavourable deviation upon complexation. It is therefore likely that the energy in the angles of TPOPO complex is not as well minimized as it should be. Energy search techniques, such as torsional angle search for starting conformations and dynamics searches on the minimized complex, need to be applied on TPOPO in order to try and locate a better minimum. We note in this case that the electrostatic and Van der Waals complexation energy terms for TPOPO are favourable as is the case for the rest of the systems in Table IV.2, further indicating the error in the calculated complexation energy for TPOPO ligand.

Before closing this section, it is worth noting that some cases will show different complexation energies for the solvated and unsolvated systems. This can be judged from the solvation effects discussed earlier on whereby it was pointed out that solvation effects can alter the steric energy of the complexes to different extents depending on various factors such as the electrostatics in the molecule. This means that we can expect different solvation effects on the steric energies of the ligand and complex in some cases. Therefore a more informative evaluation of the complexation energies should include the relative solvation effects.